

# BIOSURFACTANT ENHANCED TREATMENT OF PETROLEUM OIL CONTAMINATED SOILS

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# Nomenclature

$A$	Cross sectional area of soil sample	$\text{cm}^2$
AA	Reference point	
ASTM	American Society for Testing and Materials	
ATF	Automatic transmissions fluids	
$b$	Path length of sample	cm
CEC	Cation exchange capacity	$\text{meq} / 100\text{g soil}$
CMC	Critical micelles concentration	%-mass
CONCAWE		
$C_s$	Concentration of surfactant solution	%-mass
$C_{s,CMC}$	CMC of surfactant solutions	%-mass
$DF_{MSe}$	Degree of freedom of mean square error	
DNAPL	Dense non-aqueous phase liquids	
E	Emulsion	
$e$	Void ratio	
EASW	Electrode Assisted Soil Washing	
EC	Electrical conductivity	$\mu\text{S}/\text{cm}$
$F$	Value of the $F$ table	
GC/MS	Gas Chromatographer/Mass Spectrometer	
HCB	Hexachlorobenzene	
HCl	Hydrochloric acid	
HLB	Hydrophilic-lipophilic balance	
$i$	Hydraulic gradient	
ICP	Inductively coupled plasma	
ITF	Interfacial tension	$\text{mN}/\text{m}$
$K$	Coefficient of permeability	$\text{cm}/\text{sec}$
$L$	Length of soil through which flow occurs	cm
LNAPL	Light non-aqueous phase liquids	
$L_{16}(4^5)$	Optimum condition experimental plans	
$M$	Total mass of soil sample	g
$M$	Mass of oven-dried soil	g
M	Morality	

$m$	Degree of freedom used in the prediction of $Y_i$	
$M_c$	Mass of container	g
$M_{CS}$	Mass of container and oven dry soil	g
$M_{CWS}$	Mass of water	g
$M_{CWS}$	Mass of container and wet soil	g
$M_h$	Molecular mass of the hydrophilic group	g
$M_l$	Molecular mass of the lipophilic group	g
$M_n$	Mass of soil retained on sieve number $n$	g
$M_s$	Mass of dry soil.	g
$M_w$	Mass of water	g
$M_w$	Mass of wet soil + container	
$M_1, M_2$	Concentration of solution	%-mass
$N$	Number of total experiments	
$n$	Sieve number	
$n$	Non-weathered soil samples	
$n$	Number of repetition done for an experimental combination	
$n$	Porosity	
NaOH	Sodium hydroxide	
NAPLs	Non-aqueous phase liquids	
$n_i$	Number of repetitions in the confirmation experiment	
O	Oil	
$O_i$	Initial oil in the soil before washing	g
$O_r$	Oil remaining in the soil after washing	g
$P$	Product obtained through experiment	%
$P$	Light beam radiant power that comes out of sample	KJ/second $\text{cm}^2$
ppm	Pats per million	
$P_0$	Light beam radiant power that strikes a sample	KJ/second $\text{cm}^2$
$P_n$	Cumulative mass of soil	g
PV	Pore volume	

$Q$	Volume/time relationship ( $Q = V/t$ )	$\text{cm}^3/\text{sec}$
R	Rhamnolipid	
$R_i$	Confidence limits	
RLL (R1); RRL (R2)	Blend of rhamnolipids	
S	Saponin	
S	Saponin	
S	Water saturation of soil	
$S_{\text{C,CMC}}$	Crude oil solubility at CMC	$\text{mg/liter}$
$S_{\text{C}}$	Crude oil solubilization at any concentration	$\text{mg/liter}$
SDS	Sodium dodecyl sulfate	$\text{cm/s}$
SEM	Scanning Electron Microscope	
ST	Surface tension	$\text{mN/m}$
s	Standard deviation	
USEPA	United State Environmental Protection Agency	
T	Transmittance	
$V$	Total volume of soil including voids	$\text{cm}^3$
$V$	Volume of water flowing through the soil at time $t$	$\text{cm}^3$
$V_{\text{a}}$	Volume of air (assumed to be negligible)	$\text{cm}^3$
$V_{\text{s}}$	Volume of soil particles	$\text{cm}^3$
$V_{\text{s}}$	Volume of soil	$\text{cm}^3$
$V_{\text{T}}$	Total volume of the extract	$\text{cm}^3$
$V_{\text{v}}$	Volume of voids	$\text{cm}^3$
$V_{\text{w}}$	Volume of water	$\text{cm}^3$
$V_1; V_2$	Volume of solutions	$\text{cm}^3$
v/m	Volume/mass ratio	%-mass
W	Water	
$W$	Weight of soil	g
w	Weathered soil samples	
$w$	Water content	%
$w$	Moisture content	%
w/o; o/w	Water-in-oil and oil-in-water emulsions	
$Y_i$	Performance value of the $i^{\text{th}}$ experiment	

$Z_b$	Performance statistics	
	Compressed air pressure	g/cm <sup>2</sup>
	Concentrations	ppm; %-mass
	Density	g/cm <sup>3</sup>
	Flow rate	cm <sup>3</sup> /s; ml/minute
	Length	μmm, mm, cm
	Mass	g, mg, kg
	Mass of soil	Kg, g, mg
	Shaking speed	Strokes/minute
	Stirring speed	rpm
	Temperature	°C
	Time	days, hours, minutes, seconds
	Washing temperature	°C
	Washing time	Minutes
	Wavelength	nm
	Viscosity	cm <sup>2</sup> /s
	Volume	Liter; m <sup>3</sup> ; cm <sup>3</sup> ; ml
$\alpha$	Error level	
$\varepsilon$	Molar absorptivity	
$\gamma$	Corresponding absorbance at 400-nm	
$\chi$	Concentration of oil remaining in the soil	%-mass
$\phi$	Contact angle	
$\Omega$	Decibel value of percentage value subject to $\Omega$ transformation	db
$\Delta h$	Differential height ( $\Delta h = h_x - h_y$ )	cm
$\omega$	Error	%
$\nu$	Efficiency	mN/m
$\psi$	Effectiveness	mN/m



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## Abstract

This thesis reports the experimental measurements on the ability of biological origin surfactants (i.e. biosurfactants - aescin, lecithin, rhamnolipid, saponin and tannin) on removing crude oil and a heavy fuel oil blend from various soils, through soil washing process. The greatest advantage of soil washing is that it is a physical means of separating oil from soil using water or surfactants without chemically modifying either the soil or the oil. The oil removal performance of the biosurfactants was evaluated against that of a well studied synthetic surfactant (sodium dodecyl sulphate, SDS) using water as a base case. For this purpose, different washing settings (i.e. test tubes, stirred flasks, packed column, and air bubble assisted stirred tank) were used to treat contaminated soils with high oil toxicity.

The effects of operational parameters such as washing temperature (5 to 50<sup>0</sup>C), washing time (1 to 20 minutes), concentration of surfactant solutions (0.004 to 0.5%-mass), volume of surfactant solution (5 to 20 cm<sup>3</sup>), flow rate (2 to 16 cm<sup>3</sup>/minutes), pore volume (10 to 70) and contamination history was investigated. The interaction of the surfactant solutions with the oil and soils was also investigated, which was used to explain the dominant mechanisms behind soil washing.

The contaminated soils were prepared in the laboratory by mixing the oil and soils. Two different contamination cases were considered: weathered contamination in which freshly contaminated soils were subjected to heat treatment in a fan assisted oven (simulating weathering effect in the natural hot environments), and non-weathered contamination in which contaminated soils were not subjected to any heat treatment.

The different washing techniques employed in this study yielded a novel and informative description on the selection of biosurfactants in the remediation of crude oil contaminated soils. This is believed to have major academic and industrial values for the treatment of (1) soil contaminated with oil, (2) sand produced with oil, (3) drill cuttings, (4) enhanced oil recovery, and (5) waste drilling mud and sludge from oil storage tank. In addition, the characterization of the biosurfactants in oil-water, soil-water and oil-soil systems give a general knowledge of their behaviour, which is

important in the application for effective removal of oil from soil.

Soil washing was found to have a considerable potential in removing oil from the different contaminated soils and results were comparable with those reported in literature. Oil removal by rhamnolipid was more effective than the other biosurfactants and water was effective at higher parameter levels. Further, biosurfactants can preferentially remove certain aromatic groups, which may be desirable for more rapid soil remediation. The rhamnolipid can be equally as efficient at removing oil from soil as SDS at a repeatability range of  $\pm 6\%$ . However, rhamnolipid have advantages over SDS because the use of rhamnolipid will eliminate the need for removing surfactants from effluents as their release will not damage the environment due to their safe natures. Other surfactants (bio and/or synthetic) can be blended with rhamnolipid to achieve greater performance characteristics.

In general, the stirred tank and air bubble assisted stirred tank reactors settings were more effective in removing oil from the weathered and the non-weathered contaminated soil samples. The most influential parameter on the oil removal was washing solution temperature with more than 80% of crude oil removal at 50°C.

# **1 Introduction**

The problems of crude oil and its by-products contamination in our immediate environment are well known and documented. Their removal from contaminated soils has received greater attention in recent years using physical means in separating them. However, literature searches indicated that the removal of crude oil from soil through the soil washing technique with biosurfactants is not yet well studied like those of the single or double components of the petroleum oil. This section of the thesis discusses crude oil and its fate on land, different soil treatment methods and the general objective of this work.

## **1.1 Crude oil**

The world demand for fuel has led to the exploration and production of more sources of petroleum hydrocarbon (that is, crude oil) reserves. Crude oil is a complex varied substance both in its use and composition. Crude oil and its by-products are known as non-aqueous phase liquids (NAPLs), they are fraught with hazards to human health and the earth's ecology during all stages of production, processing and consumption. Van Hamme and Ward (1999), Barathi and Vasudevan (2001) and Jokuty et al. (2000), argued that the major constituents of crude oil are grouped into four major classes; the saturated compounds, the resins, the asphaltenes and the aromatics.

The high carbon saturated compounds always exhibit irregular evaporation, dispersion, emulsification and flow pattern on land and sea. The aromatic compounds contain benzene rings in their chemical structure, which affects their evaporation rate, and solubility in water. These properties decrease as the number of benzene rings in the structure increases. Resins and asphaltenes possess similar properties. Based on the work of Jokuty et al. (2000), asphaltenes are large resins that composed of condensed aromatic nuclei, which may carry alkyl and alicyclic systems containing heteroatoms such as nitrogen, sulphur and oxygen. Metals like nickel, vanadium and iron are also associated with the asphaltenes compounds. According to Fingas (1994), asphaltenes do not appreciably evaporate, disperse or degrade, and can stabilize water-in-oil emulsions when they are present in quantities greater than 3%-mass.

The main environmental concern with crude oil and its by-products is that, if not handled carefully, they may pose significant hazards to human health and the earth's ecology. CONCAWE (1984) gives an insight that the major causes of environmental damage are due to accidental spillages and sometimes-intentional discharge of oil or oily waste to water or land. Mackey and Hodgkinson (1996), Ekundayo et al. (2001) and Onyeike et al. (2002) noted that blow-out from pipes and pumps, pipeline corruptions and transportation can also result to environmental pollution.

Another source of crude oil contamination is improper disposal of oily waste and materials collected during field operations. For instance, Bleckmann et al. (1997) and Kristian et al. (2002) share the view that collected drilling mud and drill cuttings may flood and spread during rainy season to the nearby environment. In the view of Salter and Ford (2000), this source of contamination is more predominant in the areas of on-shore productions, unlike offshore productions where waste is discharged directly into the high sea or ocean under certain government regulatory conditions. Spills or discharges into water systems often eventually end up on land. The ideal solution of course is to prevent spills or discharges but this is not always possible. The impacts of such contamination on land range from property destruction to loss of life, or it may render a place or piece of land infertile and very harmful to both man and the local ecology.

#### **1.1.1 Fate of crude oil in soil**

According to United States Department of Agriculture (USDA 1998) and other authors such as Arora (1989) and Reed et al. (2000), soil is an unconsolidated surface material that is formed from natural bodies made up of living materials, organic and non-organic materials produced by the disintegration of rocks. Studies conducted on soils by American Society for Testing and Materials (ASTM 1994), Dorn et al. (1998), Howard (2002), Okieimen and Okieimen (2002) have focused on the effects that soil types will have within our environment when polluted with crude oil and other oily related materials. Generally, soil function at its potential in an ecosystem with respect to the maintenance of biodiversity, nutrient cycling, biomass production and water quality. When contaminated with crude oil, soil will have insufficient aeration due to the displacement of air from the spaces or pores between the soil particles. Crude oil with

low-density tends to penetrate the topsoil rapidly, whereas heavier oils with higher viscosity tend to contaminate the soil more slowly resulting in greater contamination at the surface. Moreover, during the penetration process, crude oil may not change physically. However, when left in the soil for a long time and subjected to weathering it will result in clean-up difficulties.

Many properties influence the behaviour of crude oil mixed with soil. Viscosity of crude oil affects its rate of movement and the degree to which it will penetrate soil. Schramm (1992) has studied the measurement of oil viscosity and has used it to correlate with temperature. Like density, viscosity is affected by temperature: as temperature decreases, viscosity increases. Viscosity and the forces of attraction between crude oil and soil at the interface affect the rate at which oil will spread. Jokuty et al. (1995) noted that density and viscosity of oils shows systematic variations with temperature and degree of evaporation whereas, interfacial tensions do not show any correlation with viscosity.

The effects of weathering such as oxidation, evaporation, and degradation are associated with the fast progressive loss of the lighter components of crude oil. Oxidation and degradation process contributes to the change in the physical appearance of oil. If weathering persists, the physical appearance may change from fine yellow-gray sediment to a viscous dark brown-black oil and tar, culminating in a black residue. Evaporation contributes to the weathering of the crude oil. It does not occur at constant rate, initially there is rapid loss of the more volatile fractions, followed by progressively slower loss of the less volatile components. As the more volatile crude oil components evaporate the density of oil increases, which is directly proportional to time.

## **1.2 Soil treatment methods**

Soil treatment is any operation that can alter the composition of the contaminant, through chemical, biological or physical means in order to reduce the amount, and the mobility of the oil to an acceptable permissible standard. Biowise (2000) and United State Environmental Protection Agency (USEPA 2001a) have proposed various technological approaches for remediating petroleum hydrocarbon contaminated land and classified them into four main categories:

- Chemical/physical treatment, account 52% of the total remediating technologies
- Biological treatment accounting 28%
- Thermal treatment method accounting 18%
- Off-gas technologies accounting 2 %

All these treatment methods combine different techniques in achieving the final outcome.

Biowise (2000) also noted that for field scale application, some of these treatment methods destroy the contaminants, while others separate the contaminant from soil without chemically modifying them. However, due to the limited full-scale applications of the methods listed in USEPA (2001a) with respect to crude oil and other oily contaminated soils, they are termed innovative technology (USEPA (1996a), USEPA (1998) and USEPA (2001b)).

As these remediation technologies have different modes of action in treating soil contaminants, some have greater potential and some are too time consuming and not cost effective to handle certain levels of the contamination. Others do not show the desired oil removal level from soil, while some lack government regulatory approvals. For instance, with the bioremediation process, which uses micro organisms to degrade crude oil in soil, the micro organisms break down the crude oil by using them as a food source. According to USEPA (2001c) and Adeyinka and Urum (2001), the process of bioremediation is time consuming with typical end products as carbon dioxide and water. Work on this method has been widely presented by USEPA (1995b), Townsend et al. (2000), Gray et al. (2000) and Sikdar and Irvine (1998).

The process of destroying oil at high temperatures has been reported by USEPA (1991) and USEPA (2001). Incineration and thermal treatment uses heat ranging from about 400<sup>0</sup>C to 1000<sup>0</sup>C to volatilise and combust petroleum hydrocarbon contaminants in soil. This process is expensive, though it can reduce the volume and concentration of contaminants in soil to a permissible standard, but can produce harmful waste streams. Thus, this process may not be environmentally safe due to the production of harmful by-products.

Hussein and Terry (2002) carried out studies on the process of treating crude oil contaminated soils with the aid of plants (i.e. phytoremediation). This treatment method has been noted by USEPA (2001d) to be expensive and time consuming as well. It is also affected by climatic and environmental factors.

Solidification/stabilisation may also be used; this may reduce the mobility of oil and hazardous substances in the environment through both physical and chemical means. According to USEPA (1996a), this process physically binds or encloses contaminants within a stabilised mass.

The soil washing method desorbs contaminants in fine soil particles thus separating them from bulk soil in water-based system using water or surface-active agents (i.e. surfactants) to enhance the treatment process. USEPA (1996c), USEPA (1996b), USEPA (2001f), USEPA (2001e), USEPA (1996c), share the view that, the process of soil washing is cost effective and not time consuming. They also argue that soil washing have the potential to treat and recover large volumes of contaminants at the same time.

Generally, soil treatment through the chemical/physical categories uses physical means of operations that have certain governmental and environmental regulations that makes them more acceptable. Soil washing is grouped under this category. It uses a physical means to extract and separate the contaminants from the soil, thereby reducing the quantity of contaminant. Oil removed from soil through this process can be recycled while the soil can be applied for other purposes.

The soil-washing process has been used in the United States of America to remediate Superfund sites contaminated by petroleum hydrocarbon by-products (USEPA 1995c). Tobia et al. (1994), Griffiths (1995), Semer and Reddy (1996), Kuhlman and Greenfield (1999), Tobia et al. (1994), Griffiths (1995), Semer and Reddy (1996) and Kuhlman and Greenfield (1999) studied soil washing and proposed it to be a promising innovative remediation technology. Mann (1999) argues that the process can be applied ex-situ or in-situ, and often involves aqueous surfactant solutions to desorb and concentrate the contaminants without chemically destroying them. The need for surfactants is due to their dual nature (having both hydrophobic and hydrophilic moieties) and the inability of water to completely remove this compound from soil. USEPA (2000) reported that



this process account for more than 4% of the total soil treatment methods. This is less time consuming compared with bioremediation and phytoremediation, which are affected by climatic factors.

The naturally occurring (i.e. animal, bacterial or plant origin) surfactants are classified as biosurfactants. Biosurfactants display excellent surface activity in comparison to synthetic ones despite their bulky molecular structures. As they originate from living organisms, biosurfactants have advantages of biodegradability, easily producible from renewable resources, and possible reuse by regeneration, high specificity and less toxicity (Francy et al. (1991), Van Dyke et al. (1993) and Jain et al. (1992)). They show greater environmental compatibility and also high activity at extreme temperatures, pH, and salinity conditions. Thus, they are expected to be more effective than synthetic surfactants and can be blended with other (bio and/or synthetic) surfactants to offer desired performance characteristics. Due to their physio-chemical characteristics, biosurfactants are thus better suited to environmental applications than synthetic surfactants (Pekdemir et al. (1999), Lang and Wullbrandt (1999), Kosaric et al. (1987), Muller et al. (1993), Lang and Wullbrandt (1999), Kosaric et al. (1987) and Pekdemir et al. (1999)).

Research on biosurfactants application in washing soil contaminated with crude oil is quite limited. As crude oil is composed of complex compounds that have a low solubility and high interfacial tension with water, perhaps this makes them difficult to be separated from soil. Crude oil is hydrophobic in nature; its general characteristics in aqueous surfactant solution will remain the same as those of the single and double components of petroleum hydrocarbons. However, some variations in physical and chemical properties might exist which may be different from other NAPLs; therefore, there is need for detailed study.

### **1.3 Scope of work done**

This thesis reports the results obtained from a comprehensive laboratory scale investigation of oil removal from soil with different particle size distributions (such as  $\leq 0.002$  mm,  $\leq 0.060$  mm,  $\leq 2$  mm,  $\leq 4$  mm and 2–4 mm) using surfactant solutions. Various parameters were investigated using different washing settings (i.e. test tubes,

stirred tank reactors, packed column, and an air bubble assisted stirred tank reactors), which simulate the ex-situ and in-situ soil washing techniques.

This research aims to evaluate petroleum hydrocarbon (crude oil and heavy oil) removal efficiency in soil washing using series of aqueous biosurfactant solutions (i.e. aescin, lecithin, rhamnolipid, saponin, and tannin). The performance of the biosurfactants in removing the oil from soil will be evaluated against that of a synthetic surfactant (sodium dodecyl sulphate, SDS) and water as base case. SDS was chosen because its surface activities and potentials with non-aqueous phase liquids have been well studied by Deshpande et al. (1999) and Elvers et al. (1994). The quest for biosurfactants is due to their ease of biodegradation, low environmental toxicity compared to synthetic based surfactants. Since the washing of NAPLs (i.e. crude oil) contaminated soils with biosurfactants is not well understood at the present, this study was undertaken. Similar techniques applied by Abdul et al. (1990), Bai et al. (1997) and Zhang et al. (2001) will be employed to wash the contaminated soils in different washing settings. While it is known that the performance of the water based soil-washing method is best for soils with particle sizes greater than 2-mm (Anderson et al. 1999) therefore, in this thesis different soil size fractions were tested.

The different washing techniques employed in this study yielded novel and informative description on the selection of biosurfactants in the remediation of crude oil contaminated soils. This is believed to have major academic and industrial values for the treatment of (1) oil contaminated soil (2) sand produced with oil (3) drill cuttings (4) waste drilling mud (5) enhanced oil recovery and (6) bitumen recovery from tar sand. In addition, the characterization of the biosurfactants in oil-water, soil-water and oil-soil systems give a general knowledge of their behaviour, which is important in the application for effective removal of oil from soil.

The benefit of using biosurfactant is that it will eliminate the need for removing surfactants from effluents, as their release will not damage the environment. Biosurfactants are also expected to offer savings in material costs as they are generally more effective and have better tolerance to severe environmental conditions than those synthetic ones (Maier and Soberón-Chávez (2000), Kosaric et al. (1987), Maier and Soberón-Chávez (2000), Bertrand et al. (1994), Healy et al. (1996) and Maier and Soberón-Chávez (2000)).

The scope of this work is discussed in five chapters. This present chapter gives a general overview of different oil-contaminated soil treatment methods. A comprehensive literature review is presented in Chapter 2. Detailed description on surfactants and surfactant properties, as well as the combined effects of surfactants, soil and oil are also presented. The overview of soil washing in different settings and mechanisms of oil removal in soil washing using aqueous surfactant solutions are outlined.

Chapter 3 presents the material and equipments used, material characterizations (such as surfactant and the soil samples) and methods employed in the soil washing with different settings and determination of oil removal.

Chapter 4 presents studies on the screening of biosurfactants in removing crude oil from weathered and non-weathered soil samples. To aid the understanding of oil removal mechanisms from the soil, qualitative investigation with Scanning Electron Microscope (SEM), and gas chromatograph/mass spectrometer (GC/MS) were used. Results from detailed studies using the stirred tank reactors, the stirred tank reactor assisted with air sparging and in-situ (columns) to removed crude oil and heavy oil from contaminated soils is presented. Included in this chapter are the optimum conditions for removing crude oil from soil with the biosurfactants and the synthetic surfactant using Taguchi experimental design approach.

Finally, the main conclusions and recommendations are presented in Chapter 5. The references cited within the thesis are also presented at the end of the thesis.

## 2 Literature review

### 2.1 Introduction

Limited information was located in the literature concerning the removal of crude oil from soil through soil washing techniques. This chapter will survey the background literatures on surfactant theory and those that are relevant to soil washing. The areas focused on include general overview of surfactants, properties of surfactant that are relevant in soil washing application, state-of-the-art techniques on soil washing and mechanisms of soil washing with surfactants. As already noted in Section 1.2 about the limited availability of literature on crude oil contaminated soil washing with surfactants, the materials reviewed in Section 2.2.1 and 2.3 will form the basis for biosurfactant selection in soil washing, while the literature in Section 2.4 lead to the selection of different soil particle fractions and washing settings.

### 2.2 Surfactants

Surfactants are groups of surface-active materials that have the ability to concentrate at air-water interface. They are dual in nature because they are amphiphilic molecules that consist of both a hydrophilic head moiety and a hydrophobic tail moiety group. Surfactants are often represented diagrammatically with the head and tail group model as shown in Figure 2.1. The hydrophobic moiety groups that are oil soluble are always the alkyl hydrocarbon groups of  $C_nH_{2n+1}-$ ,  $C_nH_{2n-1}-$ ,  $C_nH_{2n+1}-C_6H_4-$ , etc, whilst the hydrophilic moiety group which are water soluble include  $-COO^-Na^+$ ,  $-SO_4^-Na^+$ ,  $-SO_3^-Na^+$ ,  $-OH^-$ , etc. Surfactants are the active ingredients found in soaps and detergents, commonly used to separate oily materials from a particular media. They increase the aqueous solubility of non-aqueous phase liquids (NAPLs) by reducing their surface or interfacial tension at air-water and water-oil interfaces.

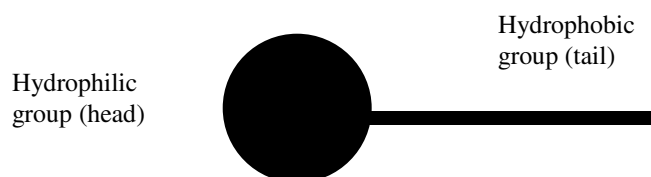


Figure 2.1. Diagrammatic representation of surfactant head and tail model

Generally, surfactants properties are best described when dissolved in aqueous solution. Surfactants are classified as ionic and non-ionic with a varying chemical structure according to their hydrophilic moiety group. For industrial applications, the ionic surfactants are classified based on the charge they carry when dissociated in water at their neutral pH. Elvers et al. (1994), Holmberg (2002) and Hummel (2000) classified the ionic surfactants as, anionic, cationic and zwitterionic or amphoteric. The anionic and cationic surfactants carry negative and positive surface-active charges, respectively, when dissociated in water. The zwitterionic or amphoteric surfactant carries both a negative and a positive charge in an aqueous solution depending on pH. The non-ionic surfactants do not dissociate into ions in aqueous solution.

Surfactants produced from chemical-based materials are known as synthetic surfactants and those from biological-based materials biosurfactants. Kosaric et al. (1987) argued that, approximately 15% of the total surfactant production is currently used in oil related applications; such as enhanced oil recovery, pipe transportation, tank cleaning, spillage treatment, bitumen recovery from tar sand, oil combustion, and de-emulsification. Surfactant applications in mineral flotation as well as pharmaceutical industries, mining, agriculture, paints and textile have been studied by Mulligan et al. (1999a), Mulligan et al. (1999b) and Knopf et al. (1994). Elvers et al. (1994), Kosaric et al. (1987), Luangpirom et al. (2001), Mittal and Kumar (2000) argued that, surfactants typical desirable properties that are useful during oil removal from soil are depends on critical micelle concentration include solubility enhancement of oil, surface tension reduction, wettability, foaming capacity and emulsion formation.

### **2.2.1 Biosurfactants**

As mentioned in Section 1.3 the naturally occurring (i.e. animal, bacterial or plant origin) surfactants are classified as biosurfactants. Kosaric et al. (1987), Bognolo (1999), Garti (1999), Biermann et al. (1987), Healy et al. (1996), studied the major classes of biosurfactants produced by microorganisms and generally grouped them into six major classes based on the producing microorganisms as: (1) glycolipids, (2) phospholipids, (3) polysaccharide-lipid complexes, (4) lipoproteins-lipopeptides, (5) hydroxylated and cross-linked fatty acids and (6) the complete cell surface

Literature such as Georgiou et al. (1992), Cassidy (2001), Chayabutra et al. (2001), Makkar and Cameotra (2001), Mata-Sandoval et al. (2001) and Lang (2002), has reported extensively on their production under different operating conditions. Bognolo (1999) argued that almost all biosurfactants are either non-ionic or anionic, as no study has reported biosurfactants with cationic structures. Ron and Rosenberg (2001) carried out studies on the micro-organisms synthesis of high (i.e. polysaccharides, proteins, lipopolysaccharides, lipoproteins) and low molecular-mass biosurfactants (glycolipids and lipopeptides) and suggested that the low molecular mass biosurfactants decrease the surface and interfacial tensions with oil, whereas the higher molecular mass biosurfactants are more effective at stabilising oil-in-water emulsions.

### **2.2.2 Surfactants applications in biodegradation**

With the growing interest of surfactants applications in environmental remediation, Billingsley et al. (1999), Evangelista et al. (1990), Noordman et al. (2002), Fu (1995), Holden et al. (2002), Huang and Lee (2001), Calvillo (1996), Hwang and Cutright (2002), Deschênes et al. (1996), Soeder et al. (1996) and Willumsen et al. (1998) have reported their use in solubilization and biodegradation of different NAPLs. Fu (1995) investigated the enhancement of biodegradation of different NAPLs by observing the effects of different surfactants, the nature of the NAPLs and agitation. The study shows that NAPLs penetrate slowly into the soil in spite of the presence of surfactant solution and the addition of surfactants at the initial stage there was no enhanced biodegradation. However, when the soil was in slurry form, rate and extent of penetration and degradation increased with some of the surfactants. In conclusion, as the contaminants were in slurry form, biodegradations of NAPLs in soil were increased by the surfactants due to intense agitation.

To evaluate the effect of surfactant concentration on biodegradation, Deschênes et al. (1996) assessed two anionic surfactants (i.e. sodium dodecyl sulfate and a biosurfactants from *Pseudomonas aeruginosa* UG2: rhamnolipid) for the biodegradation of US Environmental Protection Agency priority aged polycyclic aromatic hydrocarbons (PAH) contaminated site. They noticed that the biodegradation process was effective and rapid for the three and four ring PAH under the same test conditions, but PAHs with rings greater than four were not biodegraded under these tests conditions. Yet, the addition of a chemical surfactant hinders biodegradation. Therefore, these studies gives

an idea that the high biodegradability and the inhibitory effect of the chemical surfactants will have a significant impact on the development of both surface and in-situ soil remediation processes.

Soeder et al. (1996) also experimented on the influence of quillaya saponin and soya lecithin surfactants on the bio-removal of PAH by three bacteria in a shaken-batch culture under axenic conditions. It was noted that effective solubility of PAH was achieved at high concentrations of quillaya saponin and soybean lecithin. The complete solubilization of PAH by lecithin only doubled the maximal rate of removal of the two PAH compounds by the three bacteria (*Pseudomonas* 0259, strain MKm (*Rhizomonas*) and *Mycobacterium* EMI 2) and the bioavailability of PAH was also not improved by quillaya saponin, however, it was utilized as substrates for bacteria growth.

## **2.3 Surfactants properties**

Several properties have been used to characterize surfactants. These properties can be used to assess their suitability for soil washing. Such properties include the hydrophilic-lipophilic balance (HLB), oil solubilization capacity, emulsion formation, foaming and detergency, and interfacial and surface tensions reducing action.

### **2.3.1 Critical micelles concentration**

When there is a large concentration of surfactant solution in water there may not be enough area at the water surface for all the surfactant molecules to gather, then the surfactant will begin to cluster together in clumps called micelles. The concentration at which micelles first begin to form is known as the critical micelle concentration (CMC) as shown in Figure 2.2.

Many physical properties depend on surfactant CMC. As surfactant activities are best described in aqueous solutions, their CMC depends on temperature, surfactant chemical structure and ionic characteristics. The surfactants behaviour can be explained at concentrations below and above CMC. Holmberg (2002), Elvers et al. (1994) and Rosen (1989) made the following observations about surfactant CMC dependence on chemical structures:

- As the hydrocarbon alkyl group increases, surfactant CMC increases.

- Depending on the alkyl length the CMC of non-ionic surfactants are about two folds less than that of the ionic surfactants. However, the cationic surfactants have a higher CMC than the anionic ones.
- Increase in temperature decreases the CMC of some non-ionic surfactants whereas the solubility of ionic surfactants increases.
- Salt addition reduces the CMC of ionic surfactant while those of non-ionic are slightly affected.
- The temperature at which the solubility value of anionic surfactants equals the CMC is known as the Kraft point.
- The temperature at which cloud occur for the non-ionic surfactant solutions is known as cloud point.

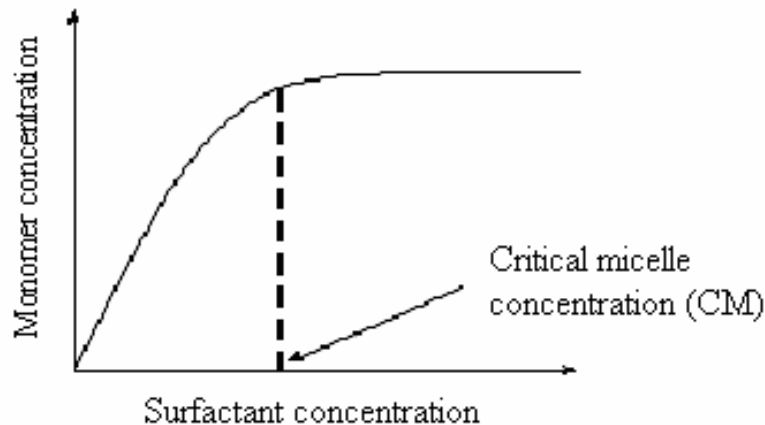


Figure 2.2. Formation of micelles at critical micelle concentration. Adopted from AATDF (1997).

### 2.3.2 Interfacial and surface tension

Surfactants will decrease the surface and interfacial tension of water-air and oil-water systems. As the interfacial tension of the oil is reduced, the capillary forces which trap or hold the NAPL in the pore space of soil are reduced. This in turn increases the mobility of oil and enhanced their separation from a porous media. Brown et al. (1994) argue that when choosing surfactant solutions for soil washing it is necessary to choose one that provides a good solubility for the oil and that solution should provide adequate reduction of the interfacial tension.



### 2.3.3 Solubilization

The aqueous solubility of oil is the apparent solubilization due to the bringing together of volume of oil and water to equilibrium, then analysing the water rich phase for oil content. The solubilization rate of single or double components of petroleum hydrocarbon components in aqueous surfactant solution can be used to assess surfactants' tendency in removing oil from a contaminated media (Bai et al. (1997), Gabr et al. (1998), Zheng and Obbard (2002), Pennell et al. (1997) and Kommalapati et al. (1997)). These authors noted that surfactant have greater capacity to solubilize polarizable hydrocarbons than extremely hydrophobic compounds such as crude oil. This seems to suggest the reason why the aqueous solubility of crude oil in surfactants has not yet been explored unlike those of the different components of petroleum hydrocarbons as noted in NAS (1985).

As surfactant solutions have both hydrophilic and hydrophobic properties: they tend to accumulate at the interfaces between water and other substances where both the hydrophobic and hydrophilic groups of its molecules have reached equilibrium (Figure 2.3). The monolayer formed at the oil–water interfaces will have the polar parts of the surfactant molecule in contact with water, and the hydrophobic parts in contact with air.

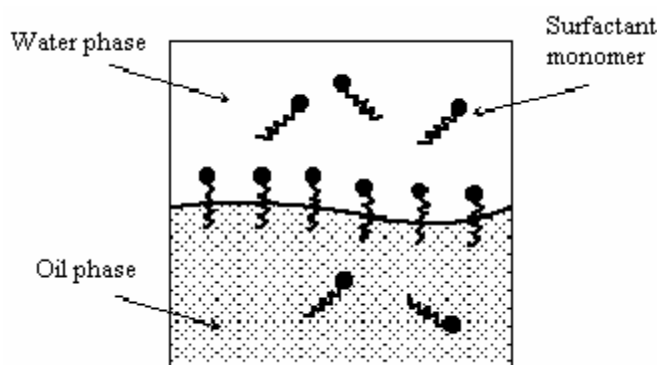


Figure 2.3. Surfactant monomer accumulation at oil-water interface. Adopted from AATDF (1997).

The oil at the water surface will be more attracted to the non-polar interior (hydrophobic group) of the micelles as shown in Figure 2.4. Micelles are often formed in relatively spherical shapes and are capable of holding oils within the interiors (Akay et al. (2000)

and Akay and Wakeman (1994)). The ability of the micelle to hold oil molecule in its interior and, because of its polar exterior (hydrophilic group), move easily through the water provides an excellent mechanism for increasing the solubility of oil molecules. This phenomenon is known as micelle solubilisation (shown latter in Figure 2.10). Micelle solubilization shows solubility that very small at concentration below surfactant CMC then rises instantaneously after reaching the CMC value.

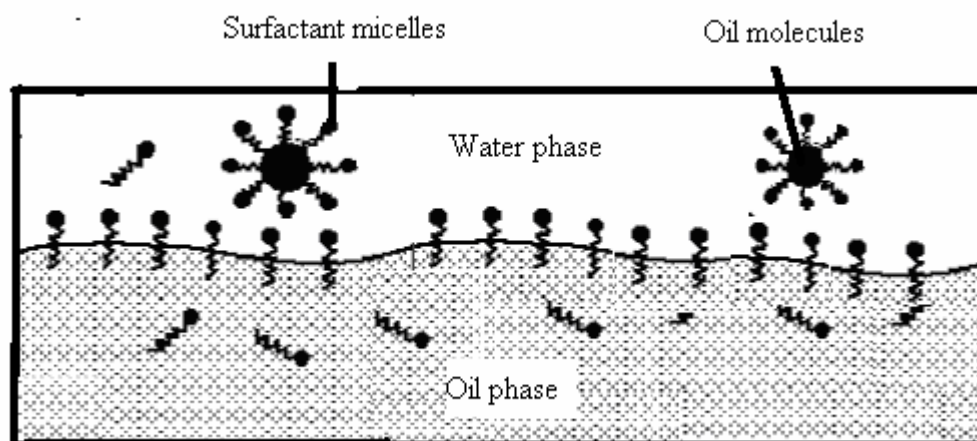


Figure 2.4. Surfactant monomers and micelles in equilibrium with oil molecules and solution interface, modify from AATDF (1997)..

#### 2.3.4 Fate of surfactants on soils

The adsorption of surfactants on soils may result in the loss and reduction of their concentration, which may render them less efficient or ineffective in soil treatment. Prior to application of surfactants to soil washing or any environmental applications, the effect and reactions on soil need to be tested. Batch and column studies have been conducted on the adsorption of anionic by Noordman et al. (2000), and non-ionic by Fortin et al. (1997), surfactants on soils. Experiment on the adsorption of different sandy soils was carried out using rhamnolipid by Noordman et al. (2000) and Witconol SN90 by Fortin et al. (1997). These two authors carried out batch studies by equilibrating soil and surfactants. The concentrations of the resulting supernatants were analysed through surface tension measurement and were compared with the concentration of the original solutions. The results of this studies suggested that the non-ionic surfactants have less adsorption tendency than the ionic surfactants. As most

soils are negatively charged in nature, the application of ionic surfactants such as the cation type will be rendered ineffective due to the resulting high sorption of the cations.

### **2.3.5 Emulsions**

Emulsions in general terms, are dispersions of oil droplets in water or water droplets in oil. When one liquid is dispersed into the other, the small droplets provide a large amount of interfacial surface area and hence greater interfacial free energy in the system. With two pure liquids, the droplets may rapidly coalesce and two separate phases will eventually form which minimize the interfacial area. Oil droplets that disperse in water are known as oil-in-water (o/w) emulsion, while water droplets dispersed in oil are known as water-in-oil (w/o) emulsions. Based on the size of dispersed phase droplets, emulsions are classified as macroemulsions (opaque in nature and have a droplet size range of 0.2 to 50  $\mu\text{m}$ ) or microemulsions (transparent or semi-transparent with particles size range of 0.01 to 0.02  $\mu\text{m}$ ).

Emulsions can be considered as solubilization of the dispersed phase in the external phase, which are insoluble in each other. This solubilization is based on the covering of the interface with surfactant that counteract coalescence of the droplets of disperse phase. The presence of surfactants can stabilize the emulsion by reducing the interfacial tension and decreasing the rate of coalescence. Such emulsions are macroemulsions to distinguish them from the thermodynamically stable microemulsions. Sjoblom (1996), Langevin (2000) and Myers (1988) studied the interfacial rheology of emulsion properties and found out that emulsions are stabilized by surfactant monolayers that adsorb at the oil–water interfaces.

The behaviour of an emulsion is related to the equilibrium phase of oil/water/surfactant system from which it is made. The combined behaviour of two immiscible liquids such as oil and water that resulted in the formation of emulsions is important in the application of surfactants in oil related environmental remediation. This is because when immiscible liquids meet a solid surface, one liquid will have the affinity to wet the solid surface in the presence of the other immiscible one. Detailed review of solid surface wetting is presented in Section 2.5.1.3. The phenomenon of wetting is important in the separation of crude oil from soil because wetting is associated with surface and interfacial tension reduction ability of surfactants.

Surfactant applications in oil contaminated site treatment often show the possibility of surfactants tending to spontaneously form emulsions between the interface of the oil and water. This behaviour has both positive and negative effects on the decontamination process. The emulsion aids in the remediation process by increasing the surface area between the water and the oil. This allows the surfactant to react easier in absorbing the oil into the micelles interior, thus increasing the mixtures solubility. If the flow of emulsions is carried easily by the surfactant, it will aid in the removal of the micelle-oil combination from the soil (Figure 2.5). However, emulsion will hinder the progression of decontamination if the emulsion viscosity becomes too thick. This will act as a barrier that isolates the oil from the surfactant. It also can clog the pore spaces in fine-grained soils, thus preventing the rapid extraction of the micelle-oil mixture.

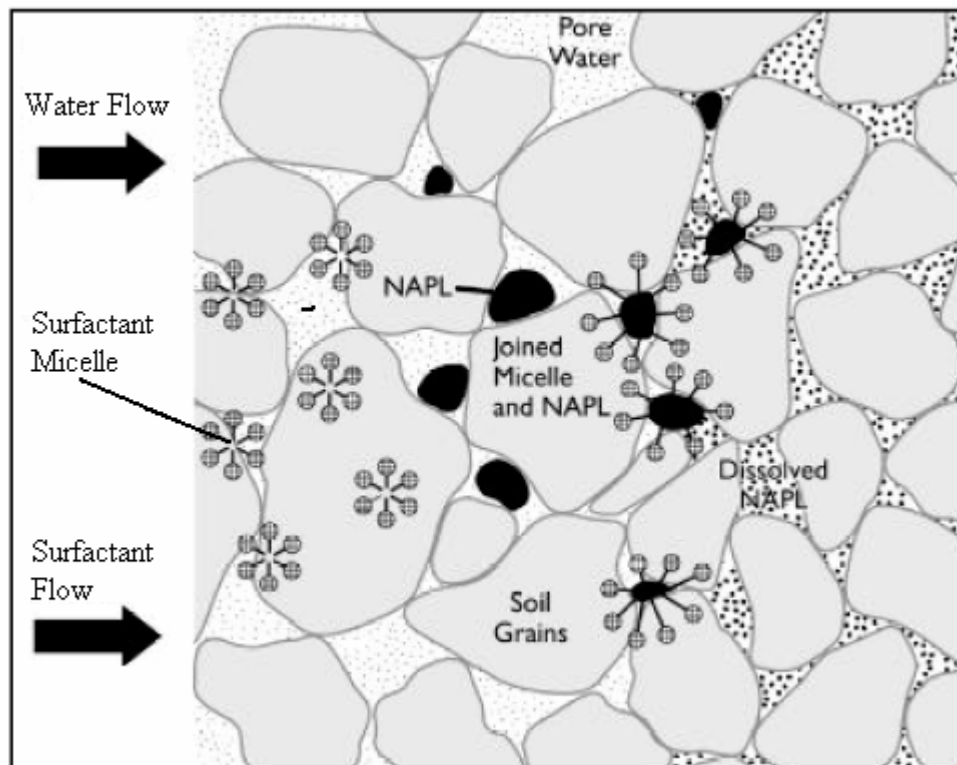


Figure 2.5. Surfactant-oil interaction.

- Water flow: the oil displaced by water from large pores can again be trapped in smaller pore spaces.
- Surfactant containing: the oil displaced by surfactant solution is dispersed and solubilized in the surfactant micelles and carried through the pore by flowing water.

Schramm (1992) studied the flow of emulsions in porous media and their influence in permeability and wettability of fluids. This author further examines the different liquid-liquid systems that stabilize emulsions in the presences or absences of surfactants and found out that emulsion formation will be detrimental during soil washing treatment. This is because emulsion formation might increase the volume of contaminant in soil. Emulsion may also have viscosity and density that are greater than that of water thus may block the flow of surfactant through soil. However, surfactant solutions that indicated greater emulsification with oil will be effective in removing oil from soil. Thus, emulsification of oil - water systems prior to the selection of surfactants for removing oil from soil is important.

Torres and Zamora (2002) investigated o/w emulsions applications in enhanced oil recovery by testing sixteen commercial surfactants with hydrophobic-lipophilic balance (HLB) values ranging from 1.8 to 18. They found out that emulsification increased as the concentration of surfactant is increased and emulsion formation depends on the reduction of surface tension which related to the surfactants HLB values.

Generally, crude oil emulsions are non-Newtonian fluids (Jokuty et al. 1995). The viscosity of emulsions is generally dominated by viscosity of the continuous phase. Thus, o/w emulsions with low oil volume fractions will behave like Newtonian fluids. Several studies have been conducted recently on the conversions of w/o to o/w emulsions, viscosity of emulsions (Fingas et al. 1999), the physics behind emulsions formation (Fingas 1995) and the long-term stability of w/o emulsions (Fingas et al. 2003). These studies showed that meso-stable emulsions will break down within three days and emulsions classified as stable will remain up to 9 years under the same laboratory conditions. Also, the density of w/o emulsions are often greater than that of water and oil which sometimes causes spilled oil to settle beneath the seabed making them very difficult during clean up. Fingas et al. (1996) also conducted rheological studies on the w/o emulsions of different crude oil. The resulting emulsions were classified on the basis of both rheological properties and visual appearance. Stable emulsions were found to have high viscosities and elasticities and are indefinitely stable. Water content appear not to relate to emulsions stability however, high or low water content does not yield a stable emulsions. Therefore, these studies suggest that the volume of surfactant solution employed for a soil washing treatment would be in appropriate ratio to the amount of oil in soil, in order to avoid the excessive formation

of emulsions which may increased the volume of contaminants needed to be removed from soil.

In emulsions stability, Mao and Marsden (1977) studied the Californian crude oil-in-water emulsions by investigating the effects of shear rate, temperature and oil concentrations and Zaki (1997) studied various factors affecting the stability and viscosity of surfactant-stabilized viscous crude-oil-in-water emulsion for pipeline transportation. The study revealed that oil-in-water emulsion stabilized by an anionic surfactant increases as the surfactant concentration increased with a subsequent decrease in the crude-oil-water interfacial tension. Generally, the oil content of the emulsions, temperature and the mixing speed affects emulsions stability and viscosity whereas, surfactant concentration and salinity of salt affects emulsions formation only. In some cases o/w emulsion can invert to w/o emulsion or vice versa due to the variation of any of these properties.

Pekdemir et al. (1999) studied the emulsification efficiency of aescin in different oil with either water or seawater. In their study, the emulsifications efficiency of aescin was compared in different systems such as seawater. Due to the effective emulsifications capacities of these surfactants, they were recommended for environmental remediation. The formation of emulsions in their study showed an indication of oil solubilisation in surfactant solutions, which could also enhance the separation of oil from soil.

### **2.3.6 Foaming**

Foams are complex fluid dispersions generally formed and stabilized by adsorbing surfactants onto fluid-fluid interface. This disperse fluid contains small bubbles that possess large surface areas which can be stabilized using surfactants. Deshpande et al. (1999) studied surfactant foaming and relates foaming stability and formation to their effectiveness in soil washing. However, their effect and relationship with soil washing have not been fully established as reports conflict (Rosen 1989). Generally, the anionic surfactants have more foaming ability than non-ionic ones because the non-ionic surfactants have a larger surface area per molecule, therefore do not have highly charged surface films in their foams. The formation of large amounts of foam will make handling the surfactant solution difficult and may not be acceptable in soil

washing process due to regulatory restrictions. However, heavy formation of foams indicates good detergency which shows surfactants effectiveness.

### 2.3.7 Hydrophilic-Lipophilic Balance

The Hydrophilic-Lipophilic Balance (HLB) enables surfactants to be arranged on a value scale from 0 to 40. This arrangement indicates the solubility and behaviour of surfactant solutions in water. Surfactants with high HLB (from about 8 to 15) are hydrophilic in nature, thus water-loving and more water-soluble. They can be used to form oil-water emulsions, with good wetting, detergency and cleaning properties. Surfactants with low HLB (i.e. between 0 to 6) are hydrophobic in nature, will partition into an oil phase and are more oil soluble. Rosen (1989), Elvers et al. (1994), Kosaric et al. (1987) argued that they are insoluble in water, form water-in-oil emulsions and act as good emulsifiers. More so, Kosaric et al. (1987) have used the HLB to assess surfactant effect in enhanced oil recovery and displacement from porous media. Results obtained through this study have been used to correlate the surfactant molecular weight, emulsification and oil recovery from different wells. Rosen (1989), Elvers et al. (1994), Sikdar and Irvine (1998) used the HLB to relate to surfactant chemical structure and emulsification then defined HLB for non-ionic surfactants as shown in Equation 2.1 as no literature reports have been cited on HLB calculation method for ionic surfactants.

$$HLB = \left[ \frac{M_h}{M_h + M_l} \right] \times 20 \quad (2.1)$$

Where,  $M_h$  is the molecular mass of the hydrophilic group and  $M_l$  the molecular mass of the lipophilic group.

Normally, the suppliers of the products always give the HLB value of surfactant solution. If the surfactants' HLB value is not known, their emulsification behaviour of the surfactant solutions is generally used to get an idea of the HLB range.

## 2.4 Soil washing techniques

Having noted in Section 1.2 that soil washing is classified under the chemical and physical soil treatment technology, this treatment method has been broadly divided into two major groups: in-situ (soil flushing) and ex-situ. The in-situ method treats the contaminated soil in place while ex-situ method treats excavated contaminated soil out of place by using different unit operations under certain operating conditions.

The traditional method of using water in the remediation of NAPLs in soil through the ex-situ and in-situ soil washing method is generally difficult due to the low solubility of NAPLs in water. According to Wilson and Clarke (1994), the application of surfactants (acts a detergent) with these technologies, can increase the rate and progress of site remediation by up to 1000-folds.

In the view of Sabatini et al. (1995) and AATDF (1997), the use of surfactant solutions has replaced the traditional pump-and-treat in-situ soil washing method normally used for the removal of NAPLs such as the light non-aqueous phase liquids (LNAPL) and dense non-aqueous phase liquids (DNAPL) from subsurface soils and aquifers. Mulligan et al. (2001c) argue that this in-situ soil washing primarily works by solubilizing the contaminants in aqueous solution, while Jafvert (1996) pointed out that this approach of soil washing can be used depending on the contaminants permissible level, volume of contaminants to be treated, governmental regulatory guidelines and the nature of site and contaminants.

The traditional ex-situ soil washing method have been studied by many researchers with increasing interest through different perspectives by Griffiths (1995), Semer and Reddy (1996), Mann (1999), Kuhlman and Greenfield (1999), Anderson et al. (1999), Bassi et al. (2000), Richardson et al. (1999), Griffiths (1995), Stinson et al. (1992), Krishnan et al. (1996) and Feng et al. (2001). They share the view that the use of water in combination with chemical additives such as alkaline and acids will desorbs, concentrate and reduce the volume of contaminants in soil for further treatment with other soil washing technology.



Stinson et al. (1992) also carried out an industrial scale soil washing to investigate a patented pilot scale soil washing process of BioTrol, Inc. The study was used to wash soil contaminated by pentachlorophenol and creosote that was generated through a wood treatment waste. These researchers applied three different technologies: 1) a volume reduction process that uses water to separate contaminated soil fractions from the soil mass, 2) a biological water treatment process and 3) a slurry bioreactor. Through this study, it was noted that more than 80 % of the two contaminants were removed from soil. This was due to the low percentage of fine soil that was less than 10 % of the total soil mass.

Griffiths (1995), reviewed different soil washing processes and described ex-situ soil washing as a volume reduction process that separates contaminants from coarse ones and concentrate them into the fine soils. Due to the limited implementation and experience in field scale applications, this author further assessed four different treatability test uses in predicting the performance of soil washing processes. The performance criteria for treating site-specific conditions were preliminary screening, remediation screening testing, remediation selection testing and remediation design testing (USEPA 1991).

In search of better soil washing solutions, the feasibility of using the soil washing process in removing mixed contaminants such as metals, volatile organic compounds, halogenated compounds, pesticides, herbicides, and insecticides from a sandy loam soil containing 66% sand and 34% silt and clay by applying different acid and isopropyl alcohol solutions have been presented by Semer and Reddy (1996). Their laboratory tests confirmed that the soil-washing process could remove the mixed pollutants from soil efficiently and economically if the washing process generation of by-products is minimized. These authors further designed and fabricated a soil-washing unit for treating the polluted soils and concluded that, effective soil washing will depend on time, type of washing solutions, contaminants and soil.

Mann (1999) conducted a pilot scale and full-scale soil washing projects with water and combinations of different chemicals. This author listed key issues to be considered for a successful soil washing project such as, the size of the project and the economic factors, soil particle size relationship with the contaminants, the nature of contaminants and regulatory situations. Also the benefits of soil washing as a cost effective remediation

method were listed. This includes the treatment method focusing only on the appropriate fractions, rather than treating the entire waste stream, handling of both organics and inorganics in the same treatment stream, a volume reduction approach that directly supports the recycle and reuse of site materials and finally, there is no air emission or wastewater discharge. The two scale of washing confirmed soil washing was a viable method for the treatment of broad range of contaminants in soil.

Kuhlman and Greenfield (1999) reviewed a soil washing process in which several unit operations such as shear mixing, spraying, hydrosizing, flotation and screening were integrated together for effective cleaning of soils. Simple and complex processes were used to illustrate the fact that soil washing is not a single process but an aggregate of unit operations operated under certain conditions to achieve a particular level of remediation. The most important conclusion from this study suggests that water could clean a variety of soils including those containing more than 30% clay water with the combination of all these treatment units.

Likewise, Feng et al. (2001) investigated the removal of diesel from a contaminated soil by using three different physical processes (i.e. jet reactor, attrition and ultrasonic washing) that cleaned contaminated soil through the transfer of the contaminant into liquid streams. In terms of technology and cost effectiveness, the laboratory studies indicated that the jet reactor was more efficient in diesel removal from soil followed by ultrasonic washing and attrition. The conclusion of this study suggested that the combination of these three washing methods will remove more than 99% diesel from the contaminated soil with approximately 0.1 mm particle size fractions.

Due to the poor removal of oil from fine soil fractions, Krishnan et al. (1996) examined the Electrode-Assisted Soil-Washing (EASW) process for washing NAPLs from contaminated soils. The EASW process was patented and results from this study showed effectiveness in removing petroleum hydrocarbons, chlorinated hydrocarbons and heavy metals from contaminated soils with high percentage of clay and silt generated by other soil-washing techniques.

### 2.4.1 Surfactant based ex-situ soil washing

Generally, the use of biological or synthetic surfactants for crude oil contaminated soil washing has not yet been fully exploited yet like those of the single or double components of petroleum hydrocarbons. Generally, reports on surfactant based soil washing showed that the oil removal process is more efficient because contaminants are separated from soil without being chemically destroyed or modified. The quest for surfactants is due to their dual nature (having both hydrophobic and hydrophilic moieties) and the inability of water to completely remove the NAPLs from soil (Mann (1999), Anderson et al. (1999), Stinson et al. (1992)). Deshpande et al. (1999), reports that the cost of using surfactants based ex situ soil washing for contaminants such as coal tar, polychlorinated Biphenyls, hydrocarbons, chlorinated hydrocarbons etc was estimated at \$50–80 per ton of soil with up to 99% contaminant removal. This cost compared favourably to other treatment processes such as bioremediation, incineration and phytoremediation whose costs ranged from \$90 to \$200 per ton.

Literature search showed that few authors such as Gatchett and Banerjee (1995) studied crude oil removal from soil with chemical surfactants while many others such as Abdul et al. (1990), Deshpande et al. (1999) and Tobia et al. (1994) have used similar chemical surfactants in removing single or double components of petroleum hydrocarbon oil from soil. However, the application of the biological surfactants in treating crude oil contaminated soil is quite limited. Further literature search have shown only the work of Harvey et al. (1990) using biosurfactant to remove crude oil from a contaminated soil.

Since crude oil is hydrophobic in nature, its characteristics in aqueous surfactant solution remain the same as those of the NAPLs, however, due to its complex nature and composition (Section 1.1), some variations in physical and chemical properties might exist which may be different from other petroleum hydrocarbon components; therefore, there is need for detailed study.

Harvey et al. (1990) tested the efficiency of a biosurfactant produced from *Pseudomonas aeruginosa*: rhamnolipid to enhance the removal of Exxon Valdez spilled oil from Alaskan gravel under various washing conditions such as temperature,

surfactant concentration and washing time. The results from the study showed that, at elevated conditions, the biosurfactant removal of the oil from soil is better than using water alone. However, the removal of oil with biosurfactant solution and water only increases as the washing temperature is increased after 30<sup>0</sup>C. The variation in contact time does not significantly enhance the removal of oil using either biosurfactant or water. The different washing conditions tested give an idea that biosurfactants have potential in crude oil removal from gravel. Also an insight of biosurfactants solution concentrations range, washing temperature and time for a soil washing process was deduced from this study.

Abdul et al. (1990) carried out a soil washing study by testing ten chemical surfactants in removing petroleum hydrocarbon oil (automatic transmission fluid) from shallow sandy aquifers. The contaminated soil had particles size up 0.5 mm and the different surfactant solutions were tested at concentrations between 0.00001 and 5 vol. %. The results from this study were used as a basis for selecting surfactants for soil washing process. Some of the conclusions in this study revealed that the removal of oil from the contaminated soil depends on the physiochemical nature of surfactant/soil/oil systems such as dispersion of oil to surfactant and surface and interfacial tension. For instance, the efficacy of the surfactant solution in reducing the interfacial tension between oil and water shows the potentials of oil removal from soil. However, certain surfactants that showed lower reduction in surface and interfacial tension does not enhance oil removal from soil. Therefore, other properties of the soil/surfactant/oil systems should be assessed for proper selection of surfactants.

Tobia et al. (1994) conducted bench-scale and pilot-scale soil washing studies in removing pentachlorophenol and creosote from soil using: 1) a commercial equipment known as the USEPA mobile volume reduction unit, 2) a non-ionic surfactant at a pH between 9 and 10, and 3) hot water at temperature of about 50<sup>0</sup>C. With the high content of sand in the contaminated soil, the washing process was effective in reducing the amount of contaminants but did not achieve the target concentration level. Besides, the results obtained through the mobile volume reduction unit gives an idea on the effects of the different parameters such as temperature, surfactant concentrations, and solid to liquid ratios to render surfactants that will be suitable for soil washing.

Gatchett and Banerjee (1995) examined a commercial scale soil washing method (Bio Genesis) by transferring a matrix of crude oil contaminants to a liquid phase using a surfactant solution, finally the surfactant solutions were used to enhance the biodegradation of the oil. The soil washing was carried out in USEPA Superfund Innovative Technology Evaluation program for soils contaminated with crude oil. The technology was able to treat about 14m<sup>3</sup> of contaminated soil at about 60°C with the surfactant solutions. However, the steps and different levels of other parameters such as mixing time, solution concentration, mixing intensity, and pH were not stated. Nevertheless, results of the studies show that about 70% of crude oil was removed from soil with the following particle size distributions 13% gravel, 76% sand, 6% silt and 5% clay.

Deshpande et al. (1999), evaluated eight surfactant solutions below and above CMC values in washing three different petroleum hydrocarbon contaminated soils. Also, these authors proposed a guideline for choosing surfactant solutions for soil washing by investigating their surface activities such as foaming, sorption capacity and solubilization effect. One of the major conclusions of this study was that the enhancement in soil washing occurred at surfactant concentrations below and above the CMC values. This showed the occurrence of both mobilization and solubilization mechanisms. Therefore, it is paramount to evaluate the surfactant solutions at concentrations below and above the CMC values for soil washing.

Bhandari et al. (2000) studied the distribution and retention of petroleum hydrocarbon, organic and inorganic materials on soil surfaces after soil washing. The soil surface was investigated qualitatively with a scanning electron microscopy and X-rays to observe the reason behind their contaminants retentions. The conclusions from this study suggested that the low hydrocarbon removal was due to the high presence of iron oxide in the soil that had the tendency of fusing soil organics and petroleum hydrocarbons. The reduction of humic acids contributes to the removal of petroleum hydrocarbon at a pH of 12 with a commercial non-ionic surfactant (Citrikleen). Therefore, it is important to assess and evaluate the characteristics of soil particle size distributions and organic materials contents in soil before the applications of surfactants in soil-washing technology.

### 2.4.2 In situ soil washing

The in-situ soil washing technique involves the remediation of contaminated soil in the place of the source contamination. Most non-aqueous phase liquids (NAPLs) contaminate the soil and then migrate into the subsurface over a period of time. If the migration persists and the soil has a large porosity the tendency of ground water to be contaminated is obvious (Figure 2.6). The main approach used in treating such contamination is the “pump and treat” system with water. The pump and treat remediation methods (i.e., water flushing) is generally considered to be ineffective due to the low water solubility of NAPLs and to mass-transfer constraints.

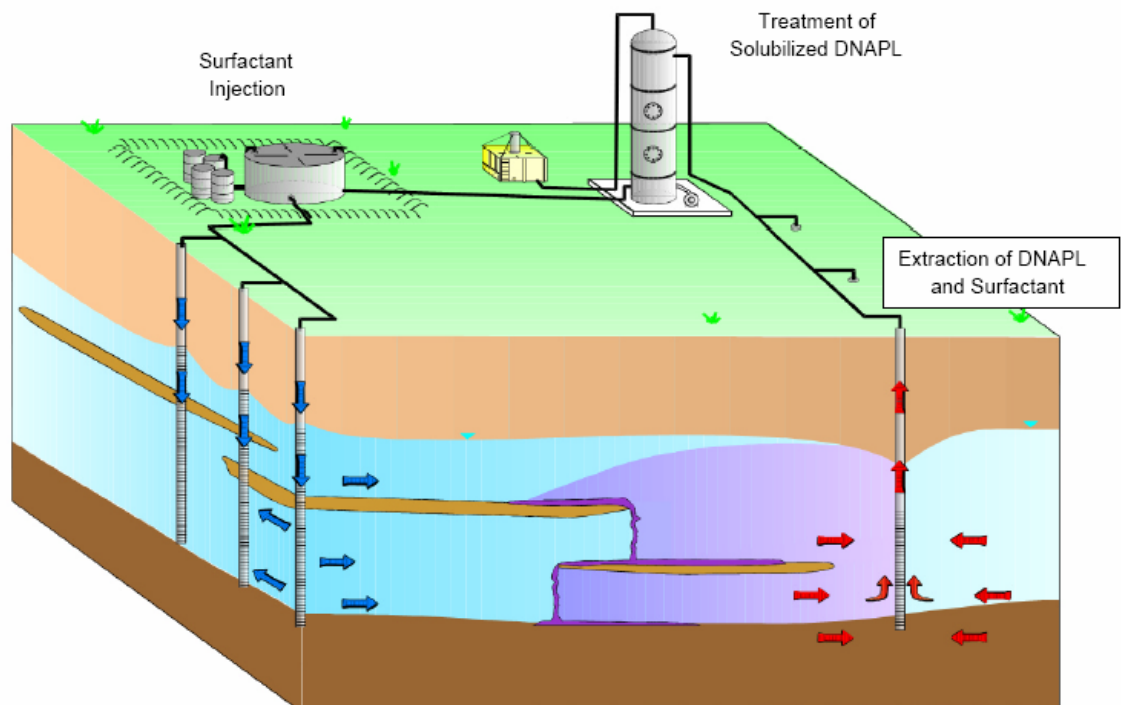


Figure 2.6. Conceptual picture of surfactant enhanced soil treatment. Adopted from USEPA (1996c).

The concept of using surfactant solutions to enhance the recovery of immiscible organic compounds from soil and ground water have been receiving considerable attention, since surfactant solutions have been used to enhance oil recovery in the late 1920s (Fortin et al. 1997). However, extension of this idea from oil recovery to aquifer remediation was only commenced in recent years. Since then, research has been done on the use of surfactants in aquifer remediation and the different aspects related to this

technique. These include sorption of surfactants on porous materials (Abdul and Gibson 1991), enhanced solubilization of hydrocarbons by surfactants (Gabr et al. 1998), surfactant selection for aquifer remediation (Abdul et al. 1990), effect of surfactants on soil (Chu and Chan 2003), biodegradation of surfactants (Ang and Abdul (1991), Kosaric et al. (1987)), and surfactant recycling (Underwood et al. (1993), Abdul and Ang (1994)).

The American Petroleum Institute API (1979) noted that knowledge of the soils and surfactants physiochemical properties will give an indication of the experimental design for surfactant-enhanced aquifer remediation. The surfactant enhanced remediation of organic chemicals has been studied both under laboratory (Abdul and Gibson 1991) and field conditions (Abdul et al. (1992), Abdul and Ang (1994)) and results from these studies, however, have often been contradictory in the sense of the dominant mechanisms behind the removal of oil from a contaminated media.

The technical feasibility of in-situ surfactant enhanced NAPLs (polychlorinated biphenyl and oils) contaminated soil washing for field scales was studied and results were compared at different pore volumes (PV) with those obtained through pilot scale study in Abdul and Ang (1994) and Abdul and Gibson (1991). The surfactant solution (alcohol ethoxylated) flows through the soil column at 1 cm<sup>3</sup>/minute at different concentration of 0.5, 1.0 and 2.0%-mass. Although the in situ method of soil washing removed oil due solubilization at greater solution concentrations, however, better oil removal was achieved with 0.5 and 1%-mass solutions. A similar study was carried out by Abriola et al. (1995) to review the extent of in-situ surfactant washing of soils contaminated specifically by dense non-aqueous phase liquids (DNAPL.). This approach of soil washing was observed to have certain limitations in treating such contaminants in soils because of the high interfacial tension between oil and water and the low solubility of water and oil. These hindrances on the economical and technical viability of in situ remediation process may be due to surface precipitation and sorption of surfactants on soils (Shiau et al. 1995).

The decontamination of subsurface soil contaminated with a light non-aqueous phase liquids (LNAPL): automatic transmission fluid (ATF) from a Superfund site have been performed using SDS by Roy et al. (1994), Roy et al. (1995) and Roy et al. (1994). An uncontaminated soil from Superfund site was air dried, homogenized, and kept in an

oven overnight at 105°C. Soil passed through a 2 mm sieve was used to pack the glass columns 10 cm long and 5.75 cm in diameter with a stainless steel top and bottom. The physical and chemical characterization of the soil was performed and the soil was classified as a fine silty loam. The glass column saturated with deionized water at a slow rate to remove the air bubbles and the water-saturated soil column allowed to drain under gravity for about 24 h. The drained column was then contaminated with ATF; the column was allowed to drain under gravity for about 24 h, beyond which the drainage was negligible. Soil flushing was conducted in down flow and up flow modes at a rate of 2.6 cm<sup>3</sup>/minute with water and surfactant solution of 2.2%-mass, which is the CMC for SDS, and a higher concentration of about 8.25%-mass and the pressure at the influent end was monitored.

The results of this study revealed that the displacement, solubilization, dispersion of ATF, and electric repulsion at the surface of the soil particles are responsible for enhanced ATF recovery. However, displacement appears to be the only mechanism that removes ATF by a water flood. Also, increasing the surfactant concentration from the CMC level to about 8.25%-mass does not increase the removal efficiency for surfactant solutions. The ATF removal in the up flow mode is higher than that in the down flow mode for water floods and is about the same for surfactant solutions. The difference in density between ATF and the washing fluid is believed to be responsible for this. The pressure drop in the case of aqueous surfactant solutions is always high (25-50psig) in both up flow and down flow conditions.

Pope and Wade (1995) summarized certain issues such as surfactants availability and behaviour that might be responsible for successful application of surfactant during in-situ soil washing based on field and laboratory scale experiment. Through this study, it was understood that the effectiveness of surfactants in field application depends on the rate limited micelles solubilization of surfactants, mobilization due to buoyancy force and the nature of soil such as permeability, porosity, surfactant low sorption ability to soil and cost.

Fountain et al. (1995) carried out a field soil washing experiment and deduced certain factors that may be responsible for successful application of in situ soil washing technology. The limitations of this technology were summarized as water chemistry,



which includes hardness, surfactant degradation, mobilization and limited solubilization of DNAPLs, surfactants sorption to soil and the soil characteristics.

Zhou and Rhue (2000) and Bourbonais et al. (1995) screened different surfactants with ionic and non-ionic surface-active moieties for in-situ washing of NAPL contaminated soils. Bourbonais et al. (1995) evaluated the capability of twenty-eight surfactants in the emulsification of the contaminants adsorbed on soils by testing their soil colloid dispersion, NAPL dispersion, solubilization and surfactants detergency at concentrations between 0.01 and 1.0% volume. Their study of in-situ soil washing in columns was conducted with four surfactants and tap water. It was known through this study that tap water was not effective in reducing poly aromatic hydrocarbons with three rings and above from the soil. However, Alcodet MC2000 (non-ionic surfactant) and Witcodet 100 (mixture of ionic and non-ionic surfactant) were more effective than the anionic surfactants in removing the contaminants from soil after passing the surfactants at different pore volumes.

Dwarakanath et al. (1999) studied variety of column experiments for selecting and evaluating suitable surfactants for remediating NAPLs in a laboratory scale. Phase behaviour experiments were used to screen food grade surfactants (i.e. sodium diamyl sulfosuccinate, sodium dihexyl sulfosuccinate and sodium dioctyl sulfosuccinate). In the phase behaviour experiment, surfactants that showed high contaminant solubilisation, fast coalescence times and the absence of liquid crystal phases and gels were selected for soil column experiment. A field soil sample composed of gravel, cobbles and sand grains was packed in a column with 4.8-cm diameter and height of either 15 cm or 30 cm. The soil column was packed with a certain mass of soil until the desired column height achieved before saturation with water. It was noted that more than 99.9% of the DNAPL could be recovered from the soil column after 2.0 pore volumes of surfactant washing. Thus, four guidelines were proposed for designing surfactant washing of soils contaminated by NAPLs.

- Phase behaviour experiments should be performed to identify surfactants with high contaminant solubilisation.
- Fast coalescence rates to classical micro-emulsions.
- Minimal liquid crystal or gel or macro-emulsion forming tendencies over the expected range of conditions.

- Low viscosity of the aqueous surfactant solution, micro-emulsion and solubilize NAPL.

Liu and Roy (1995) present an experimental investigation using SDS to remove a hydrophobic organics from soil. The relationship between the aqueous equilibrium concentration and the loss of SDS from solution with and without the presence of an electrolyte (NaCl) was established using batch and column experiments. The interactions such as adsorption, cation exchange between soil and  $\text{Na}^+$  leading to the release of  $\text{Ca}^{2+}$  and subsequent precipitation were also presented. The column soil washing experiment was also conducted to investigate the change in hydraulic conductivity due to the interactions between soil and surfactant. This study showed that the maximum amount of SDS adsorption and precipitation was observed when the concentration of SDS was in the region of the CMC and this amount was even higher in the presence of electrolyte. The injection of surfactants to a soil matrix decreases the hydraulic conductivity, and this change is related to the clay content of the soil, the type and concentration of the surfactant, and the presence of electrolyte. The amount of anionic surfactant associated with soil and precipitation increases in the presence of sodium chloride. The mechanism that is responsible for the change in hydraulic conductivity is clay expansion, sodium dispersion, fine particle mobilization and precipitation of surfactants. Therefore, in selecting surfactant for soil flushing, this should be made with considering not only the surfactant properties such as biodegradability, reusability, low CMC, and less adsorption of surfactant, but also of the interactions between surfactant and the soil matrix, amount of clay in soil which should be less than 10% clay, if the surfactant to be used is SDS.

Liu et al. (1995) investigated the interactions and transport of the surfactant (SDS) and a hydrophobic organic compound (anthracene) in the soil through in situ soil flushing process. Through this study, the equilibrium model was observed to predict the SDS breakthrough in soil columns. Mobilization of anthracene from soil column during SDS flushing was noted to be a rate-limiting process. A non-equilibrium model was found to be suitable for the prediction of anthracene breakthrough. In the soil column experiments designed to obtain the information necessary to calibrate and verify the model for the fate and transport of surfactant and anthracene through soil matrices, the transport and fate of anthracene were noted to dependent on the interactions among soil, surfactant, and the hydrodynamic conditions of the soil matrix. It was realized that the

concentrations of SDS affect the stability of anthracene in the SDS solution. Also, the process of anthracene adsorption and desorption on the soil is a rate-limited process when anthracene is in a micellized SDS solution. The non-equilibrium model is suitable for the transport of anthracene in SDS solution.

The use of plant-based surfactant extracted from fruit pericarps of *Sapindus mukorossi* (Ritha) for remediation of soil contaminated with hydrophobic organic compound (hexachlorobenzene, HCB) have been tested by Kommalapati et al. (1997) and Kommalapati et al. (1998). A glass column with dimensions 10 cm long and 5.75cm diameter was used to pack the contaminated soil following a standard procedure to achieve a bulk density similar to that of a field condition, Roy et al. (1995). The column was first saturated with de-ionized water before downward flushing with natural surfactant (concentration 0.5 and 1%-mass) and water at a flow rate of 2.5 cm<sup>3</sup>/minute. The effluent collected in each pore volume (105 cm<sup>3</sup>) was collected and analyzed for HCB. It is of interest to mention that the solubility of HCB in natural surfactant solutions increased linearly with surfactant concentration beyond the critical micelle concentration. Also, the mass of dry Ritha powder required to solubilize 1 mg of HCB in 1 liter of water was comparable to sodium dodecyl sulfate solution and other commercial surfactants. Natural surfactant solutions performed more efficiently than a simple water flood in recovering HCB from soil column washings.

It was deduced through this study that the removal of HCB started after two and five pore volumes with 1%-mass and 0.5 %-mass solutions concentration respectively. Flushing of the contaminants was terminated after the 12<sup>th</sup> pore volume, hence indicating that more HCB could be removed at higher pore volumes. HCB removal was about 80%. The surfactant solutions with concentration of 1% and 0.5% have 100 and 20 fold more removal of HCB from soil than water alone. Thus, surfactant undergoes adsorption process with soil and penetrates the surfaces between the soil and HCB more effectively than water. These studies provide a strong case for pursuing natural surfactant solutions in further research. The results of the study are crucial for determining the potential of this surfactant in remediation of contaminated soils mainly those with crude oil.

Fortin et al. (1997) performed a soil column test experiment to evaluate the effectiveness of low-concentration surfactant solution at removing a light non-aqueous

phase liquid (LNAPL) such as o-xylene and a dense non-aqueous phase liquid (DNAPL) such as o-dichlorobenzene from soil using ethoxylated alcohol (commercially known as Witconol SN90) surfactant. A glass column apparatus with dimension of 7.5-cm I.D. by 10 cm long was equipped with aluminum end plates. A screen with 0.89-mm and 0.5 mm diameter was used at the bottom and top of the column to support the porous material and to promote the spreading of the surfactant solution. It was noted that the removal of the NAPLs from the soil columns was due to solubilization, emulsification and mobilization. Due to the formation of macroemulsions during the experiments, it was suggested that the NAPL was mostly removed by immiscible displacement. Also the direction of flow was an important parameter in LNAPL removal, influencing both the location of the NAPLs in the column and the removal efficiency. These authors suggested that the two principal limitations in using surfactant solutions for in-situ soil washing is clogging of pores due to dispersion of soil particles by surfactant solution, which results in high energy consumption and lower soil permeability; and low surfactant recovery, which adds to the cost of the operation and can create further contamination of the soil with the surfactant.

From the results of this study, it is clear that a better understanding of surfactant-oil-soil interactions is necessary before this technology can be applied safely and economically for in-situ cleanup of contaminated sites. The solubilization mechanisms generally involve a series of steps, which may include interface sorption, micelle dissociation/re-formation, micelle diffusion, and simple organic species diffusion. Mobilization and dissolution/emulsification are also important processes, which need to be taken into account.

Bai et al. (1997) evaluated the potentials of a mono-rhamnolipid biosurfactant (produced by *Pseudomonas aeruginosa*) to remove residual LNAPL ( $^{14}\text{C}$ -hexadecane) saturation from sandy porous media and to determine the role of solubilization and mobilization in residual removal. The surfactant concentrations ranged [0.040 to 1.5 %-mass which is equivalent to  $(0.8 - 30) \times \text{CMC}$ ] used in this study are much lower than those used in other environmentally related studies, where they generally range from 0.5 to 4% (Ang and Abdul 1991). In a series of column experiments operated with more than 120 pore volumes of solutions, residual  $^{14}\text{C}$ -hexadecane saturation was established by pumping  $^{14}\text{C}$ -hexadecane into water-saturated sand columns and then flushing with

water at a velocity of 25 cm/h. The mono-rhamnolipid solutions were then applied to the columns at a velocity of 15cm/h to remove the residual  $^{14}\text{C}$ -hexadecane.

The primary mechanism for residual removal was mobilization (displacement and dispersion), whereas solubilization was found to be insignificant. The optimal concentration for  $^{14}\text{C}$ -hexadecane removal was at 0.5 %-mass, a concentration where both displacement and dispersion appeared to contribute to mobilization. This was approximately ten times its CMC. The removal efficiency was dependent on both the average particle size of the sand and on biosurfactant concentration. Also about 84% of the residual was removed from the column packed with coarse sand, and 22% was removed from the fine sand column. Furthermore, the performance of mono-rhamnolipid was compared with that of two synthetic surfactant solutions at 0.5%-mass. SDS (0.2 X CMC) and polyoxyethylene (20) sorbitan monooleate (38 X CMC) removed 0% and 6.1% of the residual saturation respectively. This suggested that the use of microbial surfactants might offer advantages over synthetic surfactants in remediation of contaminated sites. These laboratory-scale results indicate potential for rhamnolipid in remediation; however, many other factors will have to be considered in application of rhamnolipid on a field-scale. These include ionic strength of the soil solution, the type of cations present, and porous medium properties such as clay and organic matter content.

Of all these studies, none have made an attempt in using the in-situ soil flushing techniques in removing crude oil from either surface or sub surface soil. Therefore, some part of this thesis will be devoted in the removal of crude oil and a heavy oil from soil using the ideas gained from the in situ soil washing.

### **2.4.3 Flotation washing**

The method of flotation is used in the area of mineral processing, where hydrophobic particles are efficiently separated by air bubbles from hydrophilic base minerals with addition of surfactants or froths (concentrate foams). This process is used commercially for removal of bitumen from oil bearing sands (Schramm 1996). Two types of flotation techniques exist in literature, column flotation (Kho and Sohn 1989) and froth flotation. Mahne (1971) compared the results of both units and concluded that the performance of both units was comparable. As most available flotation books deal with mineral

flotation (Svarovsky (1990) and Leja (1982)) rather than with soil decontamination, other limited reports in the literature have shown that significant amount of petroleum oil may be removed from contaminated soil by flotation process (Zhang et al. (2001), Somasundaran et al. (1997), Chou et al. (1998) and Varadaraj (1995)). However, investigations on removal of crude oil from soil by flotation have not been reported.

When using flotation to remove oily contaminants from sediments, a surfactant is used in a manner that resembles a detergent. Most organic contaminants are naturally hydrophobic, and the objective in using a surfactant is to reduce the hydrophobicity of the oil phase to the point where it will be wetted by the water phase and detach itself from soil surfaces. The result of this is that the overall hydrophobicity of the oil phase is decreased.

The process of froth flotation relies on the differences in the wettability at solid particle-surfaces. As discussed in Section 2.5, solid surfaces are often naturally wettable by water loving (aqueous surfactant solution) termed hydrophilic while surface that is non-wettable is water repelling and termed hydrophobic (that is oil). If a surface is hydrophobic, it is also typically air attracting, and is strongly attracted to an air interface, which readily displaces water at the solid surface. Thus, in flotation process, the separation of contaminated oil from soil may also be accomplished by the selective attachment of hydrophobic oil to air bubbles (foams) and the hydrophilic particle remain in the water phase.

The flotation apparatus is schematically shown in Figure 2.7. The stirrer provides continuous mixing of the contaminated soils and surfactant solution. The sparging of compressed air is introduced into the washing vessel through the bottom. The introduction of air creates air bubbles where the oil will adhere. The difference in the density between the air bubbles and water provides buoyancy that preferentially lifts the hydrophobic oil to the surface where they remain entrained in foams which can be drained off or decanted away, thus, effecting the separation from soil (Fuerstenau and Herrera-Urbina 1989).

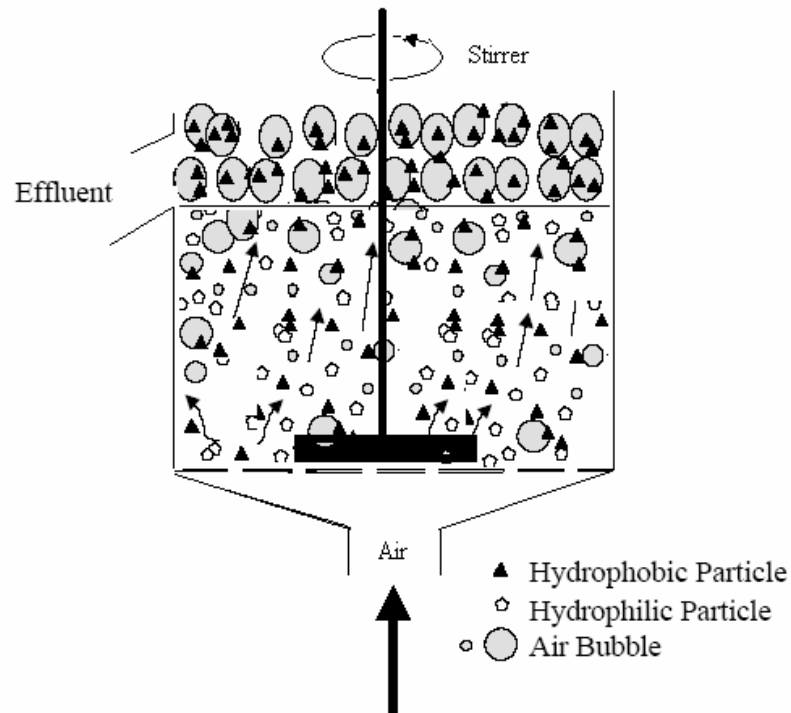


Figure 2.7. Schematic illustration of air-sparging assisted stirred tank reactor

Varadaraj (1995) presented work on the decontamination of hydrocarbon-contaminated soils through froth flotation process. Since soil will contain different amount of contaminant on the coarse particles in contrast to that on the fine particles, the contaminated soils was first separated by wet sieving into coarse and fine fractions (0.38mm). The fine soil was treated differently with a hydrocarbon solvent followed by an aqueous surfactant solution. The coarse fractions were subjected to froth flotation process with 250 cm<sup>3</sup> of a 0.5 %-mass of a commercial surfactant (EXXAL 12-7) and air sparged through the flotation vessel for 1 hour. The soil washing process was able to reduce the contaminant level in coarse soil from 3.65 to 0.8 %-mass. The author recommended that flotation in soil washing should be applicable to contaminated soil with coarse fractions. However, if the approach of flotation is used for fine particles soils, there is a great possibility of the formation of undesirable emulsions.

Somasundaran et al. (1997) investigated the feasibility of using flotation process to remove non-volatile hydrophobic compounds (paraffin oil) from artificially contaminated soil (particle size 0.075 to 0.83) using sodium dodecyl sulphate. The effect of different parameters such as flotation time and surfactants dosage in oil

removal was studied. The results of this study indicated that soil washing through flotation with 0.1 %-mass solution is effective in reducing the amount of oil in soil in comparison with the ex situ soil washing method which showed 50 % less oil removal at concentration of 0.5 %-mass. The author concluded that the low oil removal during the ex situ soil washing may be due to the small size of particles in the soil sample used. Also, flotation showed an advantage over the ex-situ soil washing (without flotation) because of the low concentration of surfactant used and the reduction of the possibility of foaming stable emulsions. The formation of stable emulsions will be possible due to the range of fine soil fractions used which is contrary to the maximum value of 0.38 mm that was mentioned by Varadaraj (1995).

In addition, alkaline chemicals, hot water or surfactant solutions have been applied in the flotation techniques to remove hydrocarbon oil from soil by Zhang et al. (2001) and Chou et al. (1998). The author suggested that the enhanced volatilization of volatile organic compounds from ground water could be carried out through air injections to the contaminated areas. This process can be applied either in ex-situ or in-situ form depending on certain environmental criteria such as cost, remediation area and equipment and governmental regulations. Also their study indicated that flotation is effective in reducing the amount of oil in soil in comparison with the ex situ soil washing method as already noted in Somasundaran et al. (1997).

## **2.5 Mechanisms of soil washing**

While a substantial body of literature exists for surfactant enhanced remediation of different petroleum hydrocarbon components contaminated sites (Bai et al. (1997), Abdul and Gibson (1991), Abdul et al. (1992), Abdul and Ang (1994), Abdul et al. (1990), Roy et al. (1995), Roy et al. (1994), Zhang et al. (2001), Liu et al. (1995), Liu and Roy (1995) Liu (1997)), much less research has evaluated surfactant enhanced ex situ or in situ soil washing for crude oil contaminated soils.

Surfactants enhance oil removal in soil washing through two mechanisms generally known as mobilization and solubilization (Cheah et al. (1998), Fortin et al. (1997), Bai et al. (1997), Bai et al. (1998), Deshpande et al. (1999) and Mulligan et al. (2001c)). At low concentrations surfactants exist solely as monomers and no enhancement of oil solubility is generally observed. These monomers will accumulate at interfaces present



in the system such as air–water, oil–water, soil–water in Figure 2.3.

As the interfacial areas are satisfied and the aqueous surfactant concentration increases the monomers aggregate to form micelles. Micelles are generally spherical in shape and can consist of several hundred individual surfactant monomers (Elvers et al. 1994)). In water, surfactant molecules will form micelles such that the hydrophilic end of the molecule faces the water, and the hydrophobic end of the molecule faces away from the water (Figure 2.4).

### **2.5.1 Mobilization**

The phenomenon associated with mobilization mechanism is the reduction of surface and interfacial tension, reduction of capillary force, wettability and the reduction of contact angle of the systems.

The mobilization mechanism occurs at concentration below the surfactant CMC (Deshpande et al. (1999) and Bai et al. (1997)). Surfactant monomers accumulate at the soil-oil and soil–water interfaces and increases the contact angle between the soil and the oil (i.e. change the wettability of the system). Surfactants in contact with the soil-oil system increase the contact angle and reduce the capillary force holding together oil and soil due to the reduction of the interfacial tension. Surfactant molecules adsorbed on the surface of the oil cause repulsion between the head group of the surfactant molecule and the soil particles, thereby promoting the separation of the oil from the soil.

Also, surfactants reduce the oil–water interfacial tension and the capillary forces that trap the residual organic. As a result, the residual oil saturation in the presence of surfactant is appreciably lower, and more oil is mobilized than with simple water floods alone. Below the CMC, solubilization does not occur, although NAPLs may reduce the CMC of surfactants in solution substantially. At the CMC, the interfacial tension of the solution is minimal and remains almost constant as surfactant concentrations increase (Abdul et al. (1990) and Rosen (1989)). The retention of oil within a given porous medium depends on the balance between viscous, capillary and gravitational forces. The mobility of trapped petroleum products increases at the CMC of aqueous surfactant solution, where the ability of the viscous force to overcome the capillary force is increased due to the decrease of interfacial tension (Ang and Abdul 1991). The

mobilized oil can either be suspended in the surfactant solution as an emulsion or be displaced and remain as a distinct non-aqueous phase.

Deshpande et al. (1999) argued that the effects of external forces of the abrasion energy generated through convective currents during shaking or agitating soil/oil systems with surfactant will lead to the exposure of more additional surface area of the oil phase to the surfactant. Through this process, adsorption between soil and surfactant can be enhanced by the displacement of oil from soil by the surfactant solution. This displacement results in the mobilisation of the oil which happens irrespective of the surfactants concentrations. The effect of temperature also plays an important part in mobilization process, that is, as temperature of oil increases; the viscosity reduces, which effectively increases the interfacial contact between soil and oil.

Through all these processes there will be mobilization of oil from the soil. Due to the adsorption of surfactants on soils, the mobilization mechanism depends on the surfactants' ionic charge. In the presence of a cationic surfactant adsorption capacity with soil will be high whereas the anionic and non-ionic surfactants will exhibit low adsorption with soil. This adsorption phenomenon of surfactants affects the removal of oil from soil. The mobilization mechanisms can be viewed into two perspectives: displacement and dispersion.

#### ***2.5.1.1 Mobilization due to displacement***

Displacement is the release of oil droplets from porous media owing to a reduction in interfacial tension (Abdul and Gibson (1991) and Ang and Abdul (1991)). From a theoretical perspective, entrapped oil will undergo displacement if the interfacial tension between the soil and oil phase is reduced sufficiently to overcome the capillary forces that caused the formation of residual saturation. According to Kosaric et al. (1987), displacement is analogous to the process used in enhanced oil recovery operations in which an optimized system is designed to reduce the interfacial tension between the oil and aqueous surfactant solution phase.

### ***2.5.1.2 Mobilization due to dispersion***

Dispersion is the process in which the oil is dispersed into the aqueous phase as very small emulsions as noted by Abdul and Gibson (1991) and Ang and Abdul (1991). Emulsions are generally not thermodynamically stable. However, owing to kinetic constraints, they may remain stable for significant time periods. Dispersion is related to both the interfacial tension and the surfactant concentration, and is different from displacement in that the displacement process is only related to the interfacial tension between aqueous solution and oil phases and no emulsion forms.

### ***2.5.1.3 Wettability***

The affinity of one immiscible liquid for a solid surface in the presence of a second or third immiscible is known as wettability. Therefore, wetting is the formation of liquid-solid interface in place of air-soil interface. As illustrates in Figure 2.8, a drop of surfactant solution rests on a contaminated soil surface. The surfactant solution and the contaminant will meet on the surface at a specific angle that is referred to as the contact angle. The fluid, through which this angle is measured to be less than  $90^{\circ}$ , is referred to as the wetting phase. The other fluid, through which the angle is measured to be greater than  $90^{\circ}$ , is referred to as the non-wetting phase. Therefore, the angle between the interfaces where the two liquids meets and the soil is the contact angle ( $\phi$ ). In the event that one phase spontaneously spreads to coat the entire solid surface, the contact angle is zero and that phase is referred to as being perfectly wetted. In such cases, the non-wetting phase does not physically touch the soil surface, but is separated from the solid surface by a thin layer of the wetting phase. If the contact angle is between  $70^{\circ}$  and  $110^{\circ}$ , the system is said to exhibit intermediate wettability.

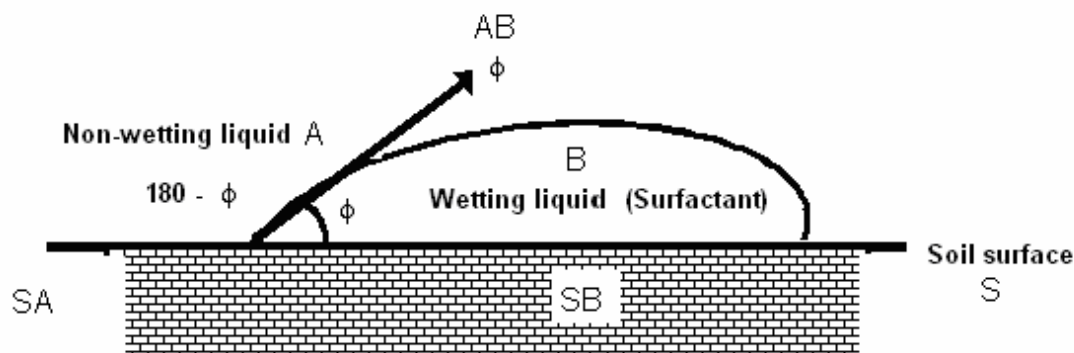


Figure 2.8. Two liquids in contact with a solid surface. The angle between the liquid interface and the solid surface is referred as contact angle. Adopted from AATDF (1997)

As most soil surfaces are negatively charged, during surfactants removal of oil from soil, the hydrophobic tail portion (oil soluble) will adsorb on the oil while the hydrophilic head (water soluble) will reside upwards in the aqueous phase. If the surfactant carries an anionic group (negatively charged ions) in aqueous solution, there will be repulsion between the surfactant molecule and the soil. This process will encourage the fast separation of oil from soil as surfactants carrying the positively charged active residue (cationic surfactants) will tend to adsorb with the soil, thereby posing the possibility of reducing the surfactants strength. However, for the non-ionic surfactants, the adsorption properties are relatively independent of the ionic solution composition because of the weak Van der Waals force between the surfactant moieties and the soil as Sardin et al. (1998) argue. Kommalapati et al. (1997) noted that the non-ionic and anionic surfactants undergo less adsorption on soil than the cationic surfactants with a positive hydrophobic group residue in solutions.

### 2.5.2 Solubilization

As mentioned earlier, the interior of a micelle constitutes a compatible environment for hydrophobic organic molecules. The process of partitioning of these molecules into a micelle in Figure 2.4 is known as solubilization (Cheah et al. 1998). The interior of a micelle is a non-polar phase and may dissolve appreciable quantities of non-polar solutes which are virtually insoluble in normal aqueous solutions.

The solubilization power of any surfactant is dependent on the ability of the surfactant to increase the apparent aqueous-phase solubility of oil. Fortin et al. (1997) argued that solubilization refers to the dissolution of the contaminant within the surfactant micelles. As the number of micelles in solution increases solubilization increases. Thus, concentrations well above the CMC are necessary for this enhancement to be significant. This mechanism has been widely studied in surfactant enhanced *in situ* soil washing by Zhou and Rhue (2000), Martel et al. (1998a), Martel et al. (1998c), Lake (1989) and Dwarakanath et al. (1999). Figure 2.9 illustrates the action of mechanisms of oil removal from soil with surfactant.

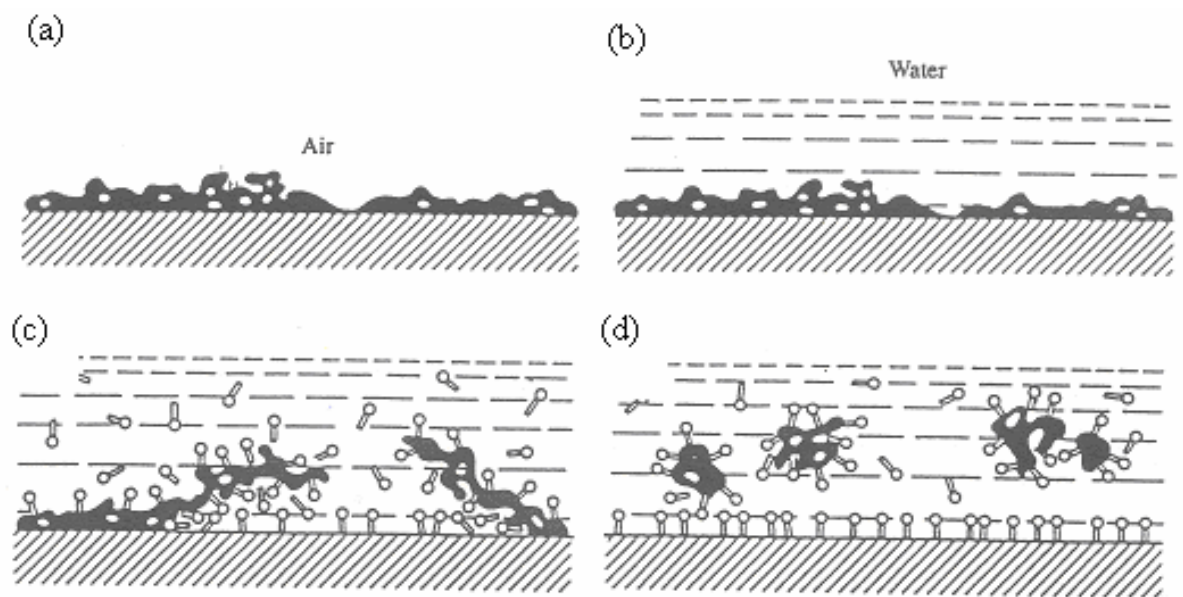


Figure 2.9. Mechanisms of oil removal from soil with aqueous surfactant solution. Adopted from Hunter (1993)

- (a) Crude oil contaminated soil
- (b) Addition of surfactant solution at low concentration
- (c) Surfactants adsorbed into all the soil surfaces: agitation or shaking creates more surface area for surfactant penetration at the interface between oil and soil
- (d) Surfactant solution at concentration above the critical micelles concentration

Figure 2.10 shows the variation of surface tension, interfacial tension and solubility of oil with surfactant solution over concentration. As concentration increases, surface and interfacial tension reduced and was constant at the CMC. Likewise, solubility increases after the CMC as the number of micelle increases in the system. AATDF (1997) then

argued that this partition into the hydrophobic core of surfactant micelles by forming oil in water emulsion would enhance the separation of oil from soil.

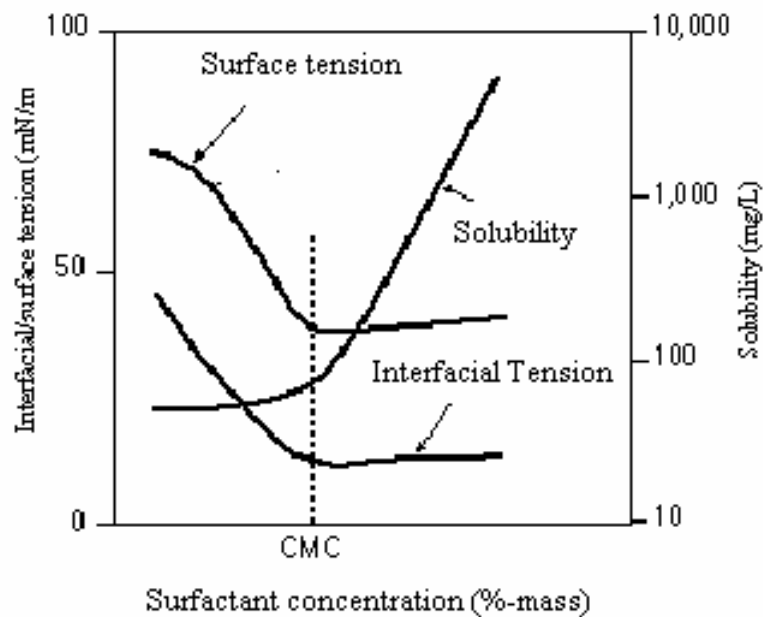


Figure 2.10. Variation of surface tension, interfacial tension and solubility of oil with surfactant solution. Adopted from AATDF (1997).

In summary, surfactant enhanced oil removal can result from the following:

- Interaction of oil with the surfactants
- Increase in contact angle between soil and oil due to wetting
- Desorption of oil from soil
- Dispersion of oil into aqueous phase
- Sorption of surfactants on soil
- Oil partitioning into the hydrophobic core of surfactant micelles

## 2.6 Seawater

The addition of an electrolytes in aqueous surfactant solutions are used under some circumstances to increase the efficiency of surfactants' oil removal from soil (Zhong et al. 2003). In the presence of electrolyte the CMC of anionic surfactants is dramatically lowered leading to the increased in the aggregation number and the micelle size as argued by Bai et al. (1998). The aggregation number of the micelle is the number of monomers in the aggregate and is dependent on the structure of the surfactant monomers. The aggregation number generally will increase when the area of the hydrophilic head group is decreased and the length of the hydrophobic tail group is increased. This effect is moderate for short chain surfactants and more pronounced for the long chain ones.

The effect of salts on the physical properties of non-ionic surfactant solution is expected to be weak with the possibility of both increase and decrease in the CMC (Holmberg 2002). The change in the CMC of non-ionic surfactants has been attributed as “salting in” and “salting out” of the hydrophobic group by the electrolyte. As noted by Rosen (1989), the energy needed to create the volume in water required to accommodate a non-polar solute is changed in salt solution because of water-ion interactions. If the work is increased in the presence of salt, the surfactant will “salt out” but if the required work is decreased the surfactant will “salt in”. When the surfactants molecules are “salted out” in the presences of salt, micelles formation is favoured and the CMC of the surfactant is decreased, however, during “salt in” the CMC is increased.

In theory, Elvers et al. (1994) mentioned that the ionic surfactants aggregate into micelles at molar concentrations that are far greater than those of the non-ionic surfactants. This is because of the electrostatic repulsion of the surfactant ions, which counteracts oriented aggregations. In the presences of salt the electrostatic repulsion of the surfactant ions is counteracted due to the increased concentration of counter-ions, thus lowering the CMC of the ionic surfactants and increased their aggregation number. Bai et al. (1998) argued that when electrolyte such as  $\text{Na}^+$  is added to a rhamnolipid solution, the  $\text{Na}^+$  would serve to screen the negative charge of the surfactant head group, effectively reducing the electrostatic repulsion between the surfactant head group. Hence the effective head group will be decreased leading to the increase in both

aggregation number of the micelles and the total interior volume of the micelle. As a result, solubilization of a non-polar compound in the micelle is increased.

Electrolyte influences the solubilization of anionic surfactants, causes precipitation of surfactant from the aqueous phases and increases their adsorption to soil. In solubilization, the addition of electrolyte anionic surfactant solution appears to increase the extent of solubilisation of hydrocarbon that are solubilized in the inner core of the micelle and decrease that of polar compounds that are solubilized in the outer portion. Increase in aggregation number of the micelles results in an increase in the hydrocarbon solubilization in the inner core of the micelle. The decrease in mutual repulsion of the ionic head group causes closer packing of the surfactant molecules in the outer layer and resulting to a decrease in the volume available for solubilization of the polar compounds.

Zhong et al. (2003) have showed that anionic surfactants such as SDS and rhamnolipid solubility and solubilization rate increase with increasing electrolyte concentration at all surfactant concentrations but for nonionic surfactant, the influence of electrolyte on the solubilization rate is insignificant, as the influence in solubility.

The understanding of the interaction between surfactant and salt and their resultant effect on surfactant performance is critical to design of a soil washing process. This will be significantly important since anionic surfactant presumably precipitate in electrolytic solutions. This is of particular interest in the field application of soil washing since soil matrix and surface solutions may contain electrolytes such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Al}^{3+}$ .



## 2.7 Surfactant phase separation

The distribution of phases and phase compositions in a surfactant – oil - water system can be represented by ternary phase diagrams. A phase is defined as a separate fluid having a characteristic density, viscosity, and chemical composition. For illustration, Figure 2.11 shows a phase diagram relating the relative volume of a particular phase to the weight percent of surfactant in a water - surfactant – oil system.

The right side of Figure 2.11, which corresponds to high SMDNS concentrations, is characterized by a separate oil phase and an aqueous phase rich in surfactant micelles containing dissolved 1,2-DCE. The micelles are composed of surfactant monomers with their hydrophobic tails pointed inward. Such systems are typically referred to as Winsor Type I, or type II (-) systems. The system is analogous to the solubilization surfactant systems in that the majority of surfactant resides in the aqueous phase, and contaminant recovery is promoted by partitioning of contaminant into surfactant micelles. This type of system has also been referred to as a single-phase microemulsion. There are two fluid phases to consider in this system (water and oil), but the surfactant micelles reside in only one of the phases (the water).

As the concentration of SMDNS is further reduced, a separate water phase will exist in equilibrium with the oil phase rich in surfactant micelles containing water. The surfactant molecules comprising the micelles are oriented with their hydrophobic tail groups pointing outward toward the oil phase. Such systems are typically referred to as Winsor Type II, or type II (+) systems. Care must be taken to ensure that a surfactant system designed as a Winsor Type I or Winsor Type III system does not shift to a Winsor Type II system in the subsurface because of the significant loss of surfactant that will occur due to partitioning into the oil phase.

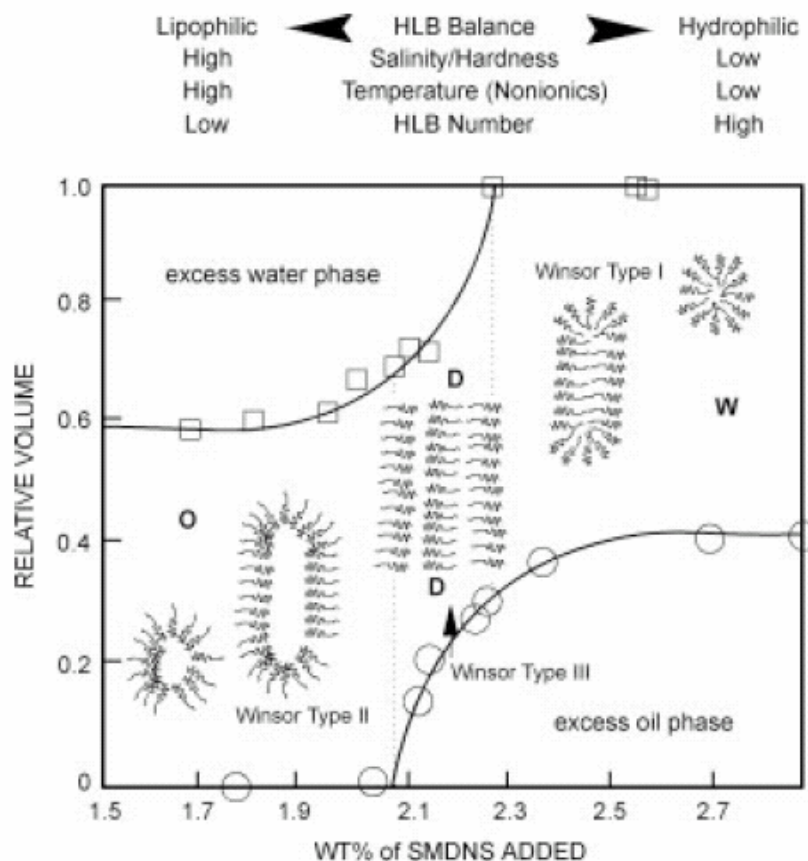


Figure 2.11. Phase diagram showing Winsor Systems (Oil and surfactant @ 15°C and 0.5%-mass). Adapted from Shiau et al., 1994.

Also Figure 2.12., illustrates ternary phase diagrams for Winsor type II (-), type III, and type II (+) systems. Each apex in these diagrams represents 100 percent composition of the labelled component. The curved surface within the type II (-) and type II (+) diagrams is referred to as the miscibility envelope or binodal curve and represents the boundary between a completely miscible, single-phase system and a two-phase system. The two phases below the miscibility envelope are taken to be a water-rich phase and oil rich phase, with surfactant distributed between the two phases. The straight lines below the miscibility envelope provide information regarding the proportion of two phases in the system and the phase compositions.

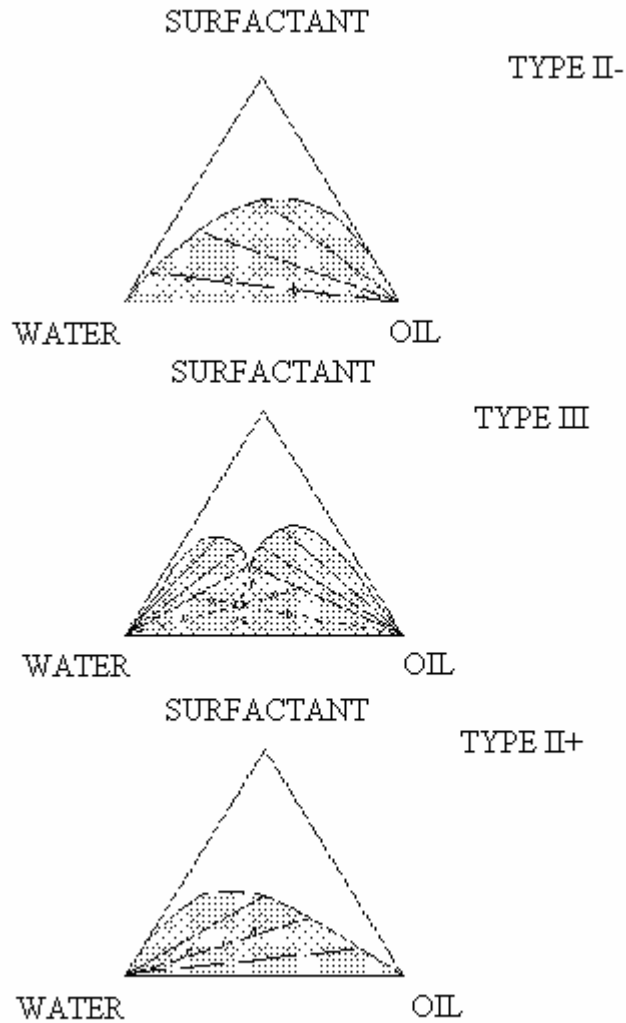


Figure 2.12. Various type of phase behaviour. Adopted from AATDF (1997)

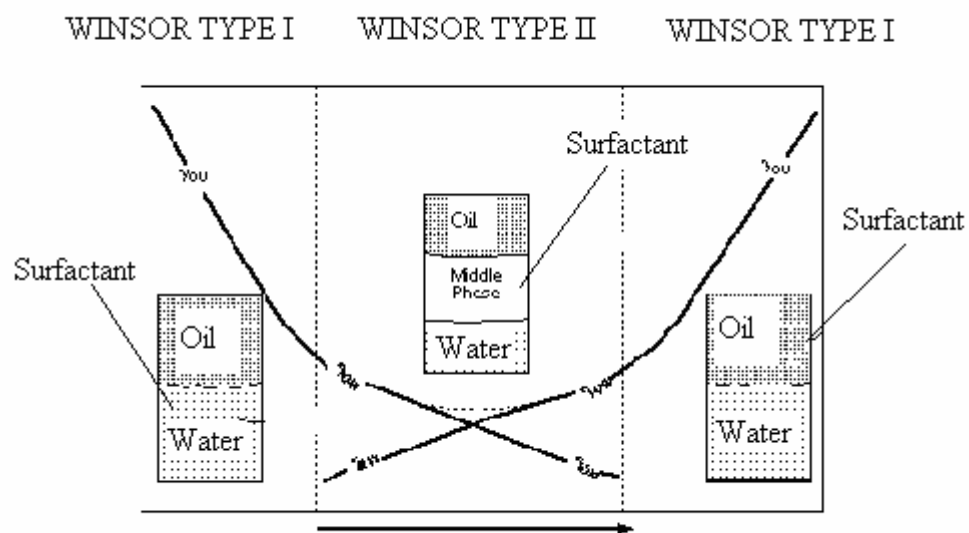
In the type II (-) system, for example, the composition of each phase is given by the composition of the endpoints of the tie lines (i.e., where they intersect the miscibility envelope). The tie lines slope down toward the oil endpoint, indicating that the surfactant partitions preferentially into the water-rich phase. The water rich phase is referred to as the microemulsion phase, consistent with the fact that this phase contains the majority of surfactant in the form of micelles. It is the type II (-) system that needs to be optimized in a solubilization surfactant enhanced soil washing applications.

In the type II (+) system, the tie lines slope down toward the water endpoint, indicating that the surfactant partitions preferentially into the oil phase. The oil rich phase is

referred to as a micro-emulsion here because it contains the majority of surfactant in the form of micelles. A type II (+) system is often undesirable because the partitioning of surfactant into the oil represents a significant surfactant loss mechanism.

In the type III system, a third-phase microemulsion is formed for system compositions within the lower triangular region below the miscibility envelope. The third phase is referred to as a microemulsion because it represents a stable mixture of oil, water, and surfactant micelles. The formation of a type III system is associated with achieving ultra-low interfacial tensions between the middle-phase microemulsion and both the water and oil phases. Type III systems are suitable for oil mobilization applications.

The variation of interfacial tension between Winsor Type I, Type II, and Type III systems is schematically shown in Figure 2.13.. The interfacial tensions decrease as either the Winsor Type I or Type II systems move toward the Type III system. The figure indicates that a shift from left to right (Winsor Type I to Type II system) will occur for increasing temperature, increasing salinity, and decreasing water solubility of the surfactant.



Increasing temperature for non-ionic surfactants; Increasing salinity for anionic surfactants; Decrease in water solubility for any surfactant

Figure 2.13. Relationship of phase behaviour and interfacial tension value. Adopted from AATDF (1997).

## 2.8 Conclusions

Soil washing using water is a reliable means of reducing the amount of contaminants in the soil by concentrating them into a smaller volume. The applications of surfactants make the removal of NAPLs more promising in terms of cost and time effectiveness. The surfactant application will lead to the mobilization and/or solubilization of oil if the surfactant concentrations are increased beyond the CMC. The removal of oil from soil that are contaminated by single and double components of petroleum hydrocarbon have been studied extensively through soil washing. In most of these studies, the steps and different levels of parameters such as mixing time, solution concentration, mixing intensity, and pH used to assessed the performances of surfactant were not stated.

Several literatures have restricted work in the remediation of subsurface soil using synthetic surfactants. The application of biosurfactant in washing soils contaminated with crude oil is quite limited. Therefore, ideas from previous studies on the treatment of NAPLs from ground water, aquifers, and sub-surfaces will be applied herein.

### **3 Materials and Methodology**

In this chapter, the materials and the equipment used to characterize the soil, surfactants and oil is presented, together with the methodology used in washing the contaminated soils.

#### **3.1 Materials**

##### **3.1.1 Soils**

The three different soils type with varying chemical compositions used in this study were supplied by two companies. The chemical analysis and particle size distributions of the soils supplied by Hepworth Minerals and Chemicals limited soil are shown in Table 3.1 and 3.2, while the Silvaperlo soil supplied by Williams Sinclair Horticulture Limited, United Kingdom is presented in Table 3.3 and Table 3.4. The Williams Sinclair soil is a horticultural grade, lime free, washed and graded quartzite grit sand with maximum nominal size of 5-mm.

In the subsequent sections of this thesis, this soil samples were classified into five different fractions (Section 3.2.1.2) according to particle size distributions as: Soil - 1, Soil - 2, Soil - 3, Soil - 4 and Soil - 5.

Table 3.1. Chemical analysis and particle size distributions of Hepworth Minerals and Chemicals limited soil (Soil - 1)

## MINERAL PRODUCTS DIVISION

### PRODUCT INFORMATION

#### MILLISIL 800

<u>Typical Chemical Analysis %</u>		<u>Limit %</u>
SiO <sub>2</sub>	98.4	98.0 Min
Fe <sub>2</sub> O <sub>3</sub>	0.055	0.090 Max
Al <sub>2</sub> O <sub>3</sub>	0.55	
Cr <sub>2</sub> O <sub>3</sub>	0.0004	
K <sub>2</sub> O	0.35	
Na <sub>2</sub> O	0.04	
LOI	0.32	

#### Typical Particle Size Distribution

<u>Microns</u>	<u>% Passing</u>	<u>Limit %</u>
40	100.0	
20	100.0	
15	99.0	
10	97.0	
5	89.0	80.0 Min

Whiteness Index	71%
Surface Area (Rigden)	19500 cm <sup>2</sup> /gm
Bulk Density	540 kg/m <sup>3</sup> (tamped)

0194

20 kg - £ 20.90

### HEPWORTH MINERALS AND CHEMICALS LTD

MINERAL PRODUCTS DIVISION,  
MONEYSTONE QUARRY, OAKAMoor, STAFFORDSHIRE ST10 3DZ  
TELEPHONE 0538 702188 TELEX 38417 FAX 0538 702972



Table 3.2. Chemical analysis and particle size distributions of Hepworth Minerals and Chemicals limited soil (Soil – 2)

**HEPWORTH MINERALS AND CHEMICALS LTD**

**MINERAL PRODUCTS DIVISION**

**PRODUCT INFORMATION**

**OAKMOOR HPF5 SILICA FLOUR**

Chemical Analysis		Typical %	Limits %
SiO <sub>2</sub>		98.4	98.00 min
Fe <sub>2</sub> O <sub>3</sub>		0.029	0.035 max
Al <sub>2</sub> O <sub>3</sub>		0.65	0.90 max
K <sub>2</sub> O		0.35	0.55 max
Na <sub>2</sub> O		0.04	0.1 max
Cr <sub>2</sub> O <sub>3</sub>		0.0005	0.0007 max
TiO <sub>2</sub>		0.07	0.1 max
LOI		0.2	0.25 max

Particle Size Distribution	Cumulative wt %	
	Passing - Typical	Passing - Limits
microns		
250	99.0	40-60
150	90.0	
125	83.0	
105	77.5	
75	61.5	
53	50.0	
40	41.0	
30	33.0	
20	24.0	
10	12.0	
5	5.0	

**Typical Properties**

**Specific Surface Area**

Rigden Method cm<sup>2</sup>/gm 1650

**Bulk Density (tamped) kg/m<sup>3</sup>** 1440

**Whiteness Index**

Hunter Colour

X	Y	Z	L	a	b	Whiteness Index	ASTM(E313) Whiteness index
74.9	75.7	81.2	89.7	1.4	5.8	47.6	

**Oil Absorption** 20 gms / 100 gms BS3483 : Part B7 : 1982

The information contained in this sheet does not constitute a specification, but is issued in good faith. A specification can be issued if required.

12/89

HEPWORTH MINERALS AND CHEMICALS LTD Brookside Hall, Sandbach, Cheshire CW11 0TR Tel: 01270 752 752 Fax: 01270 752 753



**HEPWORTH MINERALS AND CHEMICALS**

A DIVISION OF HEPWORTH PLC

HEPWORTH MINERALS AND CHEMICALS LTD, Brookside Hall, Sandbach, Cheshire CW11 0TR





Table 3.3. Chemical analysis of Silvaperlo soil supplied by Williams Sinclair Horticulture Limited, United Kingdom

**REDLAND AGGREGATES LTD.**  
**NORTHERN REGION**  
**WHITWELL LABORATORY**  
**SOUTHFIELD LANE**  
**WHITWELL, WORKSOP**  
**NOTTS, S80 3LJ**

**Redland**  
**AGGREGATES**

### AGGREGATE PROPERTY REPORT

**SOURCE: BESTHORPE**  
**MATERIAL: GRITSAND**

**REF No: BEST/5.3/95**  
**DATE SAMPLED: 18/05/95**

Chloride Content		<0.01%
Total Sulphate Content		0.03%
Relative Density: Oven Dry Basis		2.65
Saturated & Surface Dry		2.65
Apparent		2.65
Water Absorption		0.2%
Acid Soluble Material	+800µm	2.0%
	-600µm	1.0%
Bulk Density: Uncompacted		1740kg/m <sup>3</sup>
Compacted		1810kg/m <sup>3</sup>

### CHEMICAL ANALYSIS (XRF METHOD)

SAMPLE CALCINED AT 1000°C

SiO <sub>2</sub>	91.38	K <sub>2</sub> O	0.69
TiO <sub>2</sub>	0.11	Na <sub>2</sub> O	0.15
Al <sub>2</sub> O <sub>3</sub>	1.93	P <sub>2</sub> O <sub>5</sub>	0.10
Fe <sub>2</sub> O <sub>3</sub>	3.99	SO <sub>3</sub>	0.00
CaO	0.94	Mn <sub>3</sub> O <sub>4</sub>	0.01
MgO	0.69	ZnO	0.01
SrO	0.00	ZrO <sub>2</sub>	0.04
BaO	0.04	Cr <sub>2</sub> O <sub>3</sub>	0.08
V <sub>2</sub> O <sub>5</sub>	0.00	LOSS OF IGNITION	1.72

**ISSUED BY: R.C. ALLOTT**

**DATE ISSUED: 06/07/95**

*R.C. Allott*

CONTROLLED  
DOCUMENT  
CATEGORY

Table 3.4. Chemical analysis of Williams Sinclair Horticulture Limited, United Kingdom soil

## TEST REPORT

**Material:** Sample of sand submitted by Redland Aggregates Limited

**Order Number:** 70223

**Type of Test:** PETROGRAPHIC EXAMINATION OF AN AGGREGATE IN ACCORDANCE WITH THE DEPARTMENT OF TRANSPORT SPECIFICATION FOR HIGHWAY WORKS: 1991 CLAUSE 1704.6 AND APPENDIX G

**Date of Examination:** 27th June 1994

**Sample Reference:** BESTHORPE

**Particle Size Distribution:** Not required

**Lithological Types:**

(% volume)	Quartz (vein)..... 62.2	Igneous & Metamorphic..... 0.7
	Quartzite..... 24.8	Ferruginous Sandstones..... 4.6
	Limestone..... 1.4	Shell..... 0.0
	Chert..... 2.1	Feldspars..... 0.0
	Sandstone..... 0.0	Miscellaneous..... 0.7
	Oxides..... 3.5	

**Strained Quartz:** < 2.0%

**Opal, Tridymite & Cristobalite:** Trace (less than 0.1%)

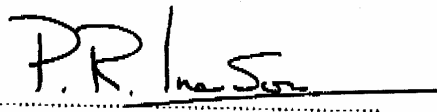
**Roundness Index:** Sub-rounded natural sand

**Clay minerals:** Nil

The sample of sand examined is non-reactive as defined in Clause 1704.6

(Note: A sampling certificate was not supplied)

FAO:- Mr K Blackburn  
Redland Aggregates Limited  
Southfield Lane  
Whitwell  
Worksop  
Notts S80 3LJ

  
Eur Ing PR Ineson  
B.Sc., Ph.D., D.Sc., C.Eng., FIMM, FGS

### 3.1.1.1 Water (moisture) content

The soil water content can be defined as the ratio or percentage of mass of free water in a given mass of soil to the total mass of soil and water together. Soil water content influences the physical properties of soil such as: weight, density, oil retention and adsorption. It is one of the most significant index properties used in establishing a correlation between soil and its properties. Water in soil may occupy soil spaces thereby reducing the amount of oil that may be used to contaminate a mass of soil. Hence, soil water content will play an important role in oil contamination and recovery.

Since Soil - 1 and Soil – 2 was dried before it was supplied, the experiment of soil water content conducted in Section 3.2.1.1 was only for Soil – 4 which contain particle sizes of Soil - 3 and Soil – 5. The water content of the soil indicated that the water in the soil before contamination with crude oil was about 0.54 %. This value was small in order to influence the contamination process. The results are shown in Table 3.5.

Table 3.5. Water content of Soil - 4

	1 <sup>st</sup> trial	2 <sup>nd</sup> trial
Mass of wet soil + container, $M_{CWS}$	5150 g	5190 g
Mass of dry soil + container, $M_{CS}$	5132 g	5170 g
Mass of container, $M_C$	1605 g	1605 g
Mass of dry soil, $M_S$	3527 g	3565 g
Mass of water, $M_W$	18 g	20g
Moisture content, $w$	0.52%	0.55%

The result implied that:

- The soil is virtually dried therefore,
- Water did not occupy any pore spaces of the soil
- Water will not influence the contamination process with oil
- Water will not have any significant effect on extraction of oil from soil with n-hexane as noted in ASTM (1994).

- The soil water content of 0.54% for Soil – 4 can be generalized for Soil – 3 and Soil – 5 because these soil samples are all derived from Soil –4 through sieving.

### 3.1.1.2 Particle size distribution

The soil particle size distribution of the Hepworth Minerals and Chemicals limited soil was determined in a standard laboratory by Marven Instruments Inc and results presented in Figure 3.1. For the purpose of this work, these soils were classified as Soil – 1 and Soil – 2 respectively. Soil – 1 have a specific surface area of 19 5 cm<sup>2</sup>/g and bulk density of 0.54 g/cm<sup>3</sup> while Soil – 2 surface area and bulk density are 1 65 cm<sup>2</sup>/g and 1.44 g/cm<sup>3</sup> respectively.

The particle size distribution of the Williams Sinclair Horticulture Limited soil is outlined in Section 3.2.1.2. It was noted that more than 75% of the total soil mass was less than 2.00 mm in size, 15% was between 2 – 4 mm and 10% was greater than 4.00-mm. Soil particles greater than 4 mm was discarded and not used for further analysis because literatures survey revealed that larger soil particles contain less amount of oil. The sieved soil with particle size less than 2 mm was classified as Soil –3, the next class (Soil – 4) was the entire soil mass that passed through the 4-mm sieve and the soil with particle size between 2 – 4 mm was classified as Soil – 5.

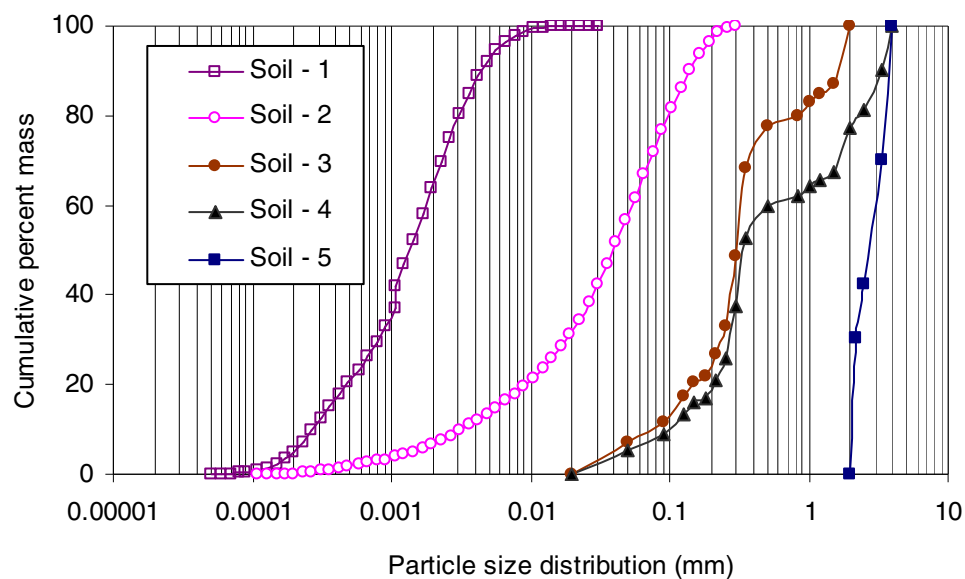


Figure 3.1. Soil particle size distributions

Texturally, Soil – 1 may be considered as clay soil with more than 60 % particles sizes  $\leq 0.002$  mm, Soil – 2 as silt soil with more than 60 % particle sizes  $\leq 0.06$  mm, Soil – 3 as fine sand ( $\leq 2$  mm), Soil – 4 as coarse sand ( $\leq 4$  mm) and Soil – 5 as gravels (2-4 mm).

### 3.1.1.3 Porosity

Porosity is an important factor to be considered in the evaluation of oil or water recovery in a soil system. It is a dimensionless quantity that indicates how much water or oil and air a soil can contain and can be correlated with the void ratio. Figure 3.2 schematically illustrates a typical soil matrix. Soil is usually made up of particles of different types and sizes. The space between particles is called pore. Pore space determines the amount of water or oil that a given volume of soil can hold. These pores are where oil may be trapped when in contact with soil. The percentage of the pore space (void volume) to the total volume of soil is known as porosity. In fluid transport study, Arora (1989) claims that porosity is used to show the differences between Darcy's velocity and the average linear velocity of fluids, through soil columns. The average linear velocity is the average velocity in the direction of flow within the soil pores.

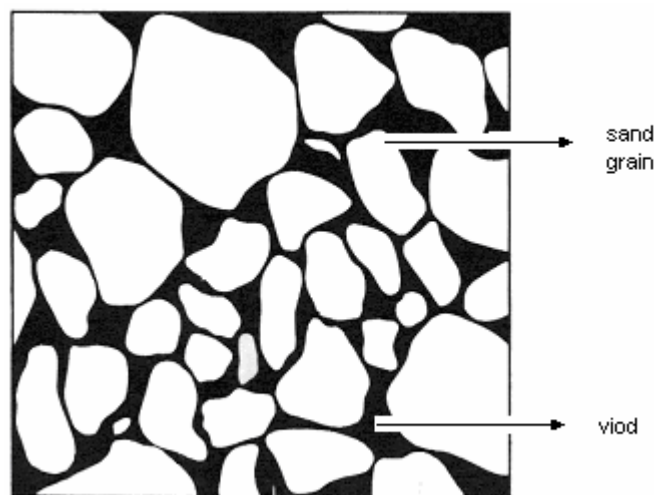


Figure 3.2. Sketch of soil sample showing solid particle and void spaces, soil particles are shown in white while voids are in black. Adopted from AATDF (1997).

The porosity of soil was performed in Section 3.2.1.3. This study was carried out for only Soil – 4. This was due to the generalised nature of the soil sample and the other

reason that it will be used for most of the soil washing studies. The void or pore spaces were first determined prior to the calculation of porosity ( $n$ ), the degree of saturation of soil with water ( $S$ ) and void ratio. Results are shown in Table 3.6 to Table 3.8 for the uncontaminated and contaminated samples of Soil – 4.

Table 3.6. Soil volume relationship with porosity, void ratio and degree of saturation of water for uncontaminated soil samples of Soil – 4

Trials	V (cm <sup>3</sup> )	V <sub>s</sub> (cm <sup>3</sup> )	V <sub>v</sub> (cm <sup>3</sup> )	V <sub>w</sub> (cm <sup>3</sup> )	n	e	S
1	120	82.00	38.00	38.00	0.32	0.46	1.00
2	120	80.00	40.00	40.00	0.33	0.50	1.00
3	120	80.00	40.00	40.00	0.33	0.50	1.00
4	120	80.00	40.00	40.00	0.33	0.50	1.00
Average	120	80.50	39.50	39.50	0.33	0.49	1.00

Table 3.7. Soil volume relationship with porosity, void ratio and degree of saturation of water for crude oil contaminated soil samples of Soil – 4

Trials	V (cm <sup>3</sup> )	V <sub>s</sub> (cm <sup>3</sup> )	V <sub>v</sub> (cm <sup>3</sup> )	V <sub>w</sub> (cm <sup>3</sup> )	n	e	S
1	120	92.00	28.00	28.00	0.23	0.30	1.00
2	120	91.00	29.00	29.00	0.24	0.32	1.00
3	120	92.00	28.00	28.00	0.23	0.30	1.00
Average	120	91.67	28.33	28.33	0.24	0.31	1.00

Table 3.8. Soil volume relationship with porosity, void ratio and degree of saturation of water for heavy oil contaminated soil samples of Soil – 4

Trials	V (cm <sup>3</sup> )	V <sub>s</sub> (cm <sup>3</sup> )	V <sub>v</sub> (cm <sup>3</sup> )	V <sub>w</sub> (cm <sup>3</sup> )	n	e	S
1	120	99.00	21.00	21.00	0.18	0.21	1.00
2	120	100.00	20.00	20.00	0.17	0.20	1.00
Average	120	99.50	20.50	20.50	0.17	0.21	1.00

As these studies were conducted with equal mass of soil (200g), results indicated that the volume of void for the uncontaminated soil was about 39.50 cm<sup>3</sup>. This was reduced to 28.88 and 20.50 cm<sup>3</sup> for crude oil and heavy oil contaminated soils indicating individual porosities of 23.60 and 17.10 % respectively. Therefore it can be argued that the porosity of the weathered soil samples of the two contaminants will not be less than 17.10 % and will not be greater than those of the non-contaminated soil with porosity of 39.50 %. The low porosity of the contaminated soils shows the adverse affects of oil on soils' mechanical and physical properties. This can contribute to the reduction in permeability and poor aeration of soil due to the displacement of soil pores with oil. The soil porosity values will be used to estimate the pore volume of surfactant during soil washing in column setting (Section 3.2.5.6).

#### **3.1.1.4 Bulk density**

Soil bulk density is the ratio of mass to the bulk volume of soil particles including the pore spaces. Variation in bulk density is attributable to the relative proportion and specific gravity of solid organic and inorganic particles and the porosity of the soil. Soil bulk density is important in quantitative soil analysis and is also used as an indicator of soil structural quality, which depends solely on the conditions of the soil structure like packing, particle size distribution and porosity.

The procedure followed for the determination of the soil bulk density is shown in Section 3.2.1.4. The results shown in Table 3.9 to Table 3.11 for the uncontaminated and contaminated soil samples of Soil – 4 indicated that the average bulk density of the non-contaminated soil is 1.64 g/cm<sup>3</sup>. This value was 0.02 g/cm<sup>3</sup> less than that obtained for both heavy oil and crude oil contaminated soils, which was within the error range of  $\pm 0.05$  g/cm<sup>3</sup>. The slight difference in bulk density is due to the increase in soil mass due to the oil, which tends to accumulate in the pores or void spaces (Figure 3.2) between the particles in the soil matrix. Therefore, the soil can stand as a replica of a typical field sample. Similarly, the soil bulk densities for Soil – 3 and Soil –5 are given in Table 3.12 to Table 3.17

Table 3.9. Soil bulk density for uncontaminated samples of Soil - 4

Trials	Mass of soil (g)	Volume of soil, V (cm <sup>3</sup> )	Bulk density (g/cm <sup>3</sup> )
1	200.00	120.00	1.66
2	200.00	123.00	1.63
3	200.00	122.00	1.64

Table 3.10. Results of soil bulk density of crude oil contaminated samples of Soil - 4

Trials	Mass of soil (g)	Volume of soil, V (cm <sup>3</sup> )	Bulk density (g/cm <sup>3</sup> )
1	200.00	120.00	1.66
2	200.00	120.00	1.66

Table 3.11. Soil bulk density for heavy oil contaminated samples of Soil - 4

Trials	Mass of soil (g)	Volume of soil, V (cm <sup>3</sup> )	Bulk density (g/cm <sup>3</sup> )
1	200.00	120.00	1.66
2	200.00	120.00	1.66
3	200.00	120.00	1.66

Table 3.12. Soil bulk density for uncontaminated samples of Soil - 3

Trials	Mass of soil (g)	Volume of soil, V (cm <sup>3</sup> )	Bulk density (g/cm <sup>3</sup> )
1	200.00	110.00	1.82
2	200.00	108.00	1.85

Table 3.13. Results of soil bulk density of crude oil contaminated samples of Soil - 3

Trials	Mass of soil (g)	Volume of soil, V (cm <sup>3</sup> )	Bulk density (g/cm <sup>3</sup> )
1	200.00	111.00	1.80
2	200.00	109.00	1.84



Table 3.14. Soil bulk density for heavy oil contaminated samples of Soil - 3

Trials	Mass of soil (g)	Volume of soil, V (cm <sup>3</sup> )	Bulk density (g/cm <sup>3</sup> )
1	200.00	110.00	1.82
2	200.00	109.00	1.84

Table 3.15. Soil bulk density for uncontaminated samples of Soil - 5

Trials	Mass of soil (g)	Volume of soil, V (cm <sup>3</sup> )	Bulk density (g/cm <sup>3</sup> )
1	200.00	140.00	1.43
2	200.00	140.00	1.43

Table 3.16. Results of soil bulk density of crude oil contaminated samples of Soil - 5

Trials	Mass of soil (g)	Volume of soil, V (cm <sup>3</sup> )	Bulk density (g/cm <sup>3</sup> )
1	200.00	140.00	1.43
2	200.00	138.00	1.45

Table 3.17. Soil bulk density for heavy oil contaminated samples of Soil - 5

Trials	Mass of soil (g)	Volume of soil, V (cm <sup>3</sup> )	Bulk density (g/cm <sup>3</sup> )
1	200.00	139.00	1.44
2	200.00	139.00	1.44

### 3.1.1.5 Particle density

The soil particle density (g/cm<sup>3</sup>) is the mass of soil divided by the volume of soil excluding the voids or pore spaces (refer to Section 3.2.1.3).

$$\text{Soil particle density (g/cm}^3\text{)} = \frac{\text{Mass of soil (M)}}{\text{Volume of soil (V}_s\text{)}} \quad (3.1)$$

Then,

$$V_s = V - V_v \quad (3.2)$$

Where  $V$  is the total volume of soil (cm<sup>3</sup>) including voids,  $V_s$  is the volume of soil particles (cm<sup>3</sup>), and  $V_v$  volume of voids (cm<sup>3</sup>).

The results of Soil – 4 particle densities are shown in Table 3.18 to Table 3.20.

Table 3.18. Soil particle density of uncontaminated soil

Trials	Mass of soil (g)	Volume of soil, $V_s$ ( $\text{cm}^3$ )	Particle density ( $\text{g}/\text{cm}^3$ )
1	200.00	82.00	2.44
2	200.00	80.00	2.50
3	200.00	80.00	2.50

Table 3.19. Soil particle density of crude oil contaminated soil

Trials	Mass of soil (g)	Volume of soil, $V_s$ ( $\text{cm}^3$ )	Particle density ( $\text{g}/\text{cm}^3$ )
1	200.00	92.00	2.17
2	200.00	91.00	2.20
3	200.00	92.00	2.17

Table 3.20. Soil particle density of heavy oil contaminated soil

Trials	Mass of soil (g)	Volume of soil, $V_s$ ( $\text{cm}^3$ )	Particle density ( $\text{g}/\text{cm}^3$ )
1	200.00	99.00	2.02
2	200.00	100.00	2.00

### 3.1.1.6 Permeability

Permeability is one of the most critical properties to be considered in the design of oil removal in soil columns. The rates of water or surfactant flow in soil columns are related directly to permeability. The effectiveness of oil removal in soil column depends upon the mobility of the surfactant solution through the soil column. Mobility is strongly controlled by the permeability of the oil and water, which in turn is dependent upon saturation of both fluids. Permeability is the proportionality constant between flow velocity and hydraulic gradient, which is referred to as flow porosity and expressed by Darcy's Law. This flow porosity is the fraction of the total porosity that is interconnected, which contributes to the overall flow of fluid through the soil sample.

The coefficient of permeability is equal to the rate of flow of water through a unit cross-sectional area under a unit hydraulic gradient. It can be influenced by soil particle size and shape, the void ratio, temperature, pressure difference existing between the two points where flow is occurring and the degree of saturation of water. Soil permeability varies with the type of soil and other properties of fluids.

As only Soil – 4 will be used for the column soil washing, its permeability was ascertained by passing water through soil columns as described in Section 3.2.1.5. When the flow of water through the soil column became constant, the volume of water discharged per time was obtained. The volume and time data at this constant flow rate was used to construct plots as shown in Figure 3.3 to Figure 3.5. The soil coefficient of permeability ( $K$ ) for the soil samples was obtained at 20°C using the hydraulic gradient ( $i$ ), volume/time ( $Q = V/t$ ) relationship from the plots, length ( $L = 9.55$  cm) and cross-sectional area ( $A = 12.57$  cm<sup>2</sup>) of soil column.

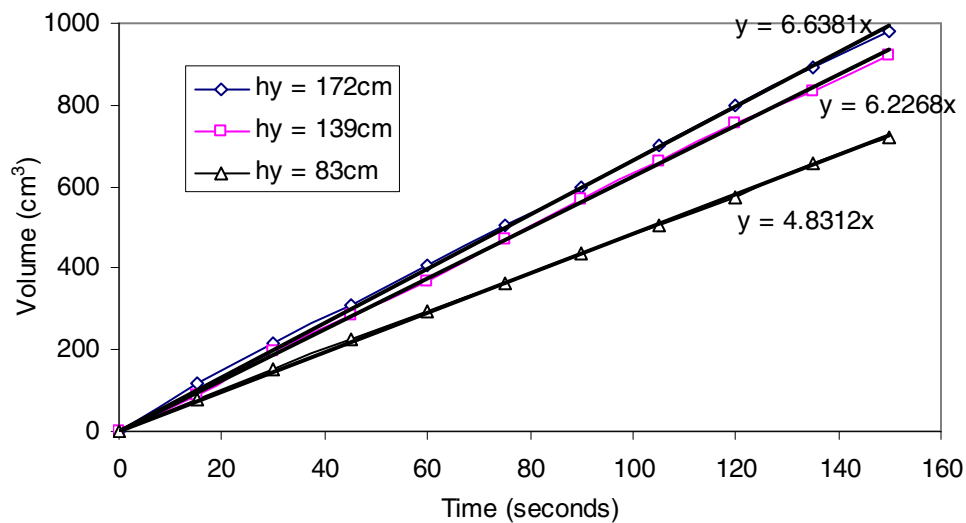


Figure 3.3. Volume and time relationship at constant outlet flow of water for non-contaminated soil sample.

Table 3.21. The coefficient of permeability ( $K$ ) for the non-contaminated sample

$\Delta h$ (cm)	$i$	$Q$ (cm <sup>3</sup> /sec)	$A$ (cm <sup>2</sup> )	$K$ (cm/sec)
128	13.40	6.64	12.57	0.040
95	9.95	6.23	12.57	0.050
39	4.08	4.83	12.57	0.093

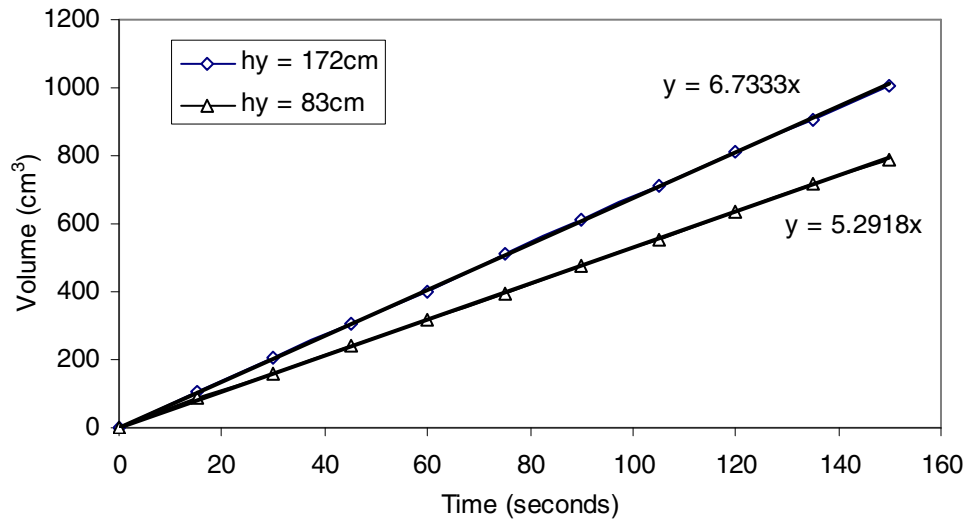


Figure 3.4. Volume and time relationship at constant outlet flow of water for crude oil contaminated soil samples of Soil - 4.

Table 3.22. The coefficient of permeability ( $K$ ) for crude oil contaminated soil sample of Soil - 4

$\Delta h$ (cm)	$i$	$Q$ (cm <sup>3</sup> /sec)	$A$ (cm <sup>2</sup> )	$K$ (cm/sec)
128	13.40	6.73	12.57	0.040
39	4.08	5.29	12.57	0.103

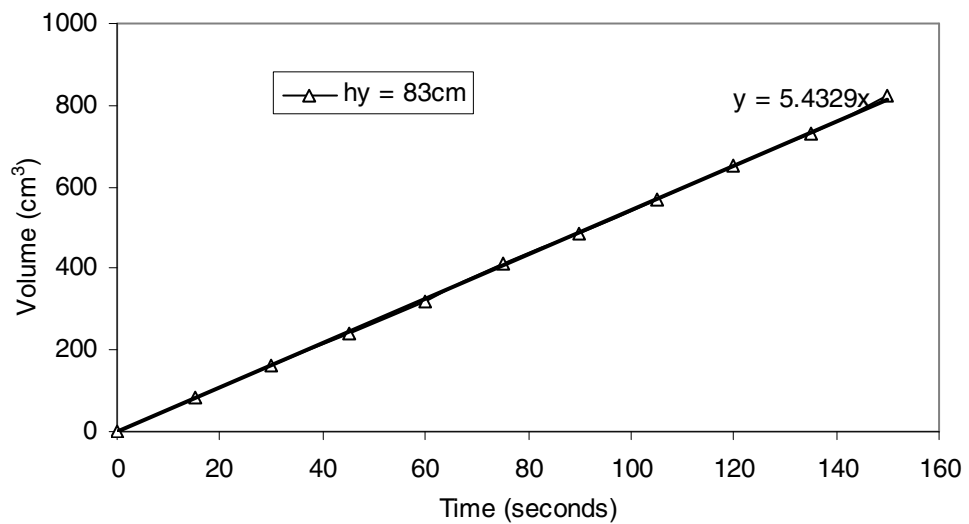


Figure 3.5. Volume and time relationship at constant outlet flow of water for heavy oil contaminated soil samples of Soil - 4.

Table 3.23. The coefficient of permeability (  $K$  ) for heavy oil contaminated soil sample of Soil - 4

$\Delta h$ (cm)	$i$	$Q$ (cm <sup>3</sup> /sec)	$A$ (cm <sup>2</sup> )	$K$ (cm/sec)
39	4.08	5.43	12.57	0.106

Since the plots in Figure 3.3 to Figure 3.5 have the same trend, the linear graph obtained after plotting volume of water discharge against time indicates that:

- The flow of water in the column was stable
- There was no air trapped in the soil samples
- There was no settling or washing out of soil particles throughout the study.
- The coefficient of permeability obtained in this work was within the range of 0.01-1.00 cm/sec. This value was within the range given by Das (1990) for coarse and medium sand.

Therefore, the above gives an indication that the soil permeability will control the mobility of surfactants or removed oil in a soil during a soil column washing.

### 3.1.1.7 pH

The pH of a soil is its measure of relative acidity or alkalinity; pH is an acronym for potential hydrogen. The soil pH was determined following the procedure in Section 3.2.1.6. The effect of soil pH is important in characterization of soil. Low pH in soil is always associated with high hydrogen ions content. In Table 3.24, all the soil samples showed a neutral pH except Soil – 2 with pH of 6.29. Therefore, the application of surfactant solutions during soil washing will not influence the acidity or alkalinity of soil samples. This will be advantageous for the soil washing studies since its main objective is to investigate the performances of the surfactant solutions at their natural properties such as pH.

Table 3.24. pH of the soil samples

Soil samples	pH value @ 18.2 <sup>0</sup> C		
	1 <sup>st</sup>	2 <sup>nd</sup>	Average
Soil – 1	7.25	7.43	7.34
Soil – 2	6.27	6.31	6.29
Soil – 3	7.07	7.14	7.56
Soil – 4	7.38	7.43	7.46
Soil - 5	7.08	7.18	7.13

#### 3.1.1.8 Cation exchange capacity

Cation exchange capacity (CEC) is a reversible process that measures the capacity of soil to hold positively charged ions (cations) such as  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $NH_4^+$ . These cations are held by negatively charged particles of clay and humus, which consist of thin and flat plates, and for their size have a comparatively large surface area. For this reason they are capable of holding enormous quantities of cation. CEC is one of the most important soil chemical characteristics that relates to soil organic matter content and clay present in the soil which is influenced by the soil pH. As the soil pH increases (becomes less acidic), the number of negative charges on soil increase due to more organic matter thereby increasing CEC. However, CEC varies according to the type of soil.

The procedure used to determine the soil CEC is described in Section 3.2.1.7. The sodium concentrations obtained from the calibration curve and the individual cation exchange capacity of soil after evaluating Equation 3.16 is given in Table 3.25.

The finer (clay) soil (Soil – 1) has larger CEC than the sandy soils (Soil – 3, Soil – 4 and Soil – 5). Clay and organic matter have negative charge, so naturally they attract positively charged materials and repel negatively charged ones. For this reason, anions find it easy to reside in soil while cations are repelled and easily leached out of the soil. Soil - 2 showed the lowest pH of 6.29, thus the CEC was expected to be higher than

7.58 *meq*/100g soil because the soil had a larger surface area and thus may have more site to be readily exchangeable in comparison to Soil – 3 and Soil – 4 with greater CEC.

Table 3.25. Cation Exchange capacity of soil samples

Soil samples	Sodium concentration (ppm)	CEC ( <i>meq</i> /100g soil)
Soil – 1	17.9	44.75
Soil – 2	3.03	7.58
Soil – 3	8.59	14.32
Soil – 4	6.10	10.17
Soil – 5	3.77	6.28

Knowledge of CEC will be useful in developing soil treatment procedures for different soils. This is because oil will tend to bind with soil that have greater amount of CEC, this will eventually lead to difficulties in separating the oil from soil. In the application of surfactants in removing oil from the contaminated soil, the pH of the surfactant solution is better to be within the pH of the soil. This approach will eliminate the possibility of accelerating CEC, if the pH of surfactant solution used is much greater. However, the time of contact between the surfactant solution and the contaminated soil is paramount.

### 3.1.2 Oils

The oils used to contaminate the soils were the North Sea Ekofisk crude oil blend and the heavy oil blend. The North Sea Ekofisk crude oil blend was referred as “crude oil” throughout this thesis and was originally supplied by STATOIL, UK, while the heavy oil blend referred to as “heavy oil” was supplied by BP oil. The important properties of these oils are shown in Table 3.26 and Table 3.27 for the crude oil and the heavy oil respectively.

The heavy oil blend composed of 80% marine residual fuel oil (MRFO) and 20% marine distillate fuel: BP marine gas oil (MDF). The MRFO is used for industrial purposes, marine and commercial boilers and furnaces, also for low and medium speed diesel engines. The chemical compositions are Fuel oil, residual oil with the following hazardous components: hydrogen sulphide (H<sub>2</sub>S), highly flammable gas and other

flammable light hydrocarbon gases.

The MDF is fuel for diesel engines or heating/boiler plant. The chemical composition is a complex mixture of middle distillate hydrocarbons, with carbon numbers in C<sub>10</sub> to C<sub>28</sub> range. The hazardous components are cracked components containing polycyclic aromatic hydrocarbon compounds may be present - Fuels and diesel.

Table 3.26. Properties of North Sea Ekofisk Crude oil blend, source from STATOIL (1999)

	Unit	Result	Method
API	°	37.7	
Specific gravity at 60/60°F		0.8362	
Density at 15°C	kg/cm <sup>3</sup>	0.8358	IP 365
Total sulphur	%-mass	0.25	IP 336 and IP 373
Hydrogen sulphide	mg/kg	<1	UOP 163
Total Acid Number	mg KOH/g	0.08	IP 177
Reid Vapor Pressure	psi	5.2	IP 69
Pour point	°C	-9	IP 15
Viscosity at 20°C	cm <sup>2</sup> /s	8.163 x 10 <sup>-2</sup>	IP 71
Viscosity at 50°C	cm <sup>2</sup> /s	3.616 x 10 <sup>-2</sup>	IP 71
Nickel	mg/kg	2.3	CBA21
Vanadium	mg/kg	1.5	CBA21
Sodium	mg/kg	0.7	CBA21
Calcium	mg/kg	1.0	CBA21
Magnesium	mg/kg	<0.1	CBA21
Ash content	%-mass	0.010	IP 4
Salt content	mg/l	72	IP 265
Wax content at -25°F	%-mass	3.73	CBA4
Water content	%-mass	0.023	IP 386
Bottom Sediments & Water	%-vol	Trace	D-4007
Pentane insolubles	%-vol	0.35	D-893
Composition:			
Methane	%-mass-	<0.01	IP 344
Ethane	%-mass	<0.01	IP 344
Propane	%-mass	0.23	IP 344
i-Butane	%-mass	0.25	IP 344
n-Butane	%-mass	1.12	IP 344
Total C1 - C4	%-mass	1.60	IP 344
i-Pentane	%-mass	1.12	IP 344
n-Pentane	%-mass	1.52	IP 344
Total pentanes	%-mass	2.64	IP 344



Table 3.27. Properties of heavy oil blend

	Units	MRFO	MDF	Test Method
Ratio		80 %	20 %	
Physical state		Liquid	Liquid	
Colour		Black	Clear	
Density @ 15°C	kg/m <sup>3</sup>	1010 max	890 (max)	ASTM D 1298
Flash point (PMC)	°C	62 min	62 min	ASTM D 93
Kinematic viscosity @ 40°C	cm <sup>2</sup> /s		1.5 – 6 x 10 <sup>-2</sup>	ASTM D 445
Kinematic viscosity @ 50°C	cm <sup>2</sup> /s	30 – 700 x 10 <sup>-2</sup>		ASTM D 445

To confirm the data provided for the oils, experiment on the viscosity and density of the oils were performed. The viscosity was determined using the Carri-Med CS Rheometer – EK01.02F at 20°C and the values obtained were:

- Crude oil: 0.08464 poise = 10.14 x 10<sup>-2</sup> cm<sup>2</sup>/s
- Heavy oil: 1.91300 poise = 189.03 x 10<sup>-2</sup> cm<sup>2</sup>/s

For the density, the test was conducted at 20°C. A calibrated flask with a volume of 61.50 cm<sup>3</sup> was measured and the weight recorded. Oil was poured in the flask and the weigh of the oil and flask recoded. The density of the oil was determined by measuring the mass of oil in the flask then divided by the volume of oil. The results are summarized in Table 3.28, which was compactable with the stated specifications.

Table 3.28. Density of oil

	Crude oil	Heavy oil
Mass of oil (g)	51.36	62.21
Volume of oil (cm <sup>3</sup> )	61.5	61.5
Density of oil (g/cm <sup>3</sup> )	0.835	1.012

### 3.1.3 Soil contamination

The soil contamination process was carried out as described in Section 3.2.2.1. Table 3.29 summarizes the quantity of oil in soil after contamination, which was determined with n-hexane extractions (refer to Section 3.2.6). n-hexane extraction was used because some of the soil and oil were lost during the contamination process due to sticking of oil at the walls of the mixing drum. Therefore, the disparity of oil initially used for contamination and those observed after the contamination are due to the loss of materials during the contamination process. For a check, 500g of Soil – 4 was contaminated in a pan dish with 50 g of crude oil. After n-hexane extraction it was noted that one-gram of Soil - 4 contained about 97.48 mg of crude oil. Therefore, n-hexane was capable of extracting more than 97 % of crude oil from soil.

Generally, the results indicate that as the soil particle size increased less oil was needed to saturate the soil. As drainage of oil on the soil could not be avoided after the contamination process, the oil saturation with soil was limited to the quantity of oil that could withstand the total mass of soil without draining.

Table 3.29. Oil content (mg) per gram of contaminated soil

Soil samples	Initial oil used (mg)	Crude oil (mg)		Heavy oil (mg)	
		Non-weathered	Weathered	Non-weathered	Weathered
Soil – 1	655.26	423.36	331.73	318.34	293.16
Soil – 2	166.00	98.95	89.87	-	-
Soil – 3	132.80	93.10	89.76	62.51	58.23
Soil – 4	99.60	91.15	86.84	53.21	45.78
Soil – 5	49.80	39.20	37.83	17.44	15.97

#### 3.1.3.1 Weathering of contaminated soils

The contaminated soils were subjected to heating in order to observe the effect of evaporation of lighter oil components from soil and to simulate the effect of exposure of contaminated soil samples to the environment after a period of time. Examples of these

situations are seen during oil spill incidents or in cases when aged crude oil contaminated soil needs remediation. The method used for the weathering process is described in Section 3.2.2.2. The soil samples that were oven treated are referred to as “weathered soil samples, w” whereas those that were not oven treated after contamination are “non-weathered soil samples, n”. The amount of oil in the weathered soil samples is also presented in Table 3.29.

As the compounds in oils vary widely in their chemical and physical properties, during the weathering part of the study different fractions were expected to be lost, depending on time of exposure and surface area of soil. As the chemical and physical nature of the oil changes, the appearance of the weathered contaminated soil changes in comparison with the non-weathered soils. As soil samples were exposed at temperature far above the oil pour point, the oil did not behave as a solid. Through the process of weathering the more volatile components of the oil were lost due to evaporation. Most of the volatile components were lost within the first 24 hours. After 14 days, the rate of evaporation decreases, as the oil in the contaminated soil was not observed to be constant shown in Figure 3.6, while Table 3.30 shows the amount of oil in the soil samples. As a control, crude oil alone was oven treated at the same conditions as the contaminated soils and percent evaporation of oil observed within the time period.

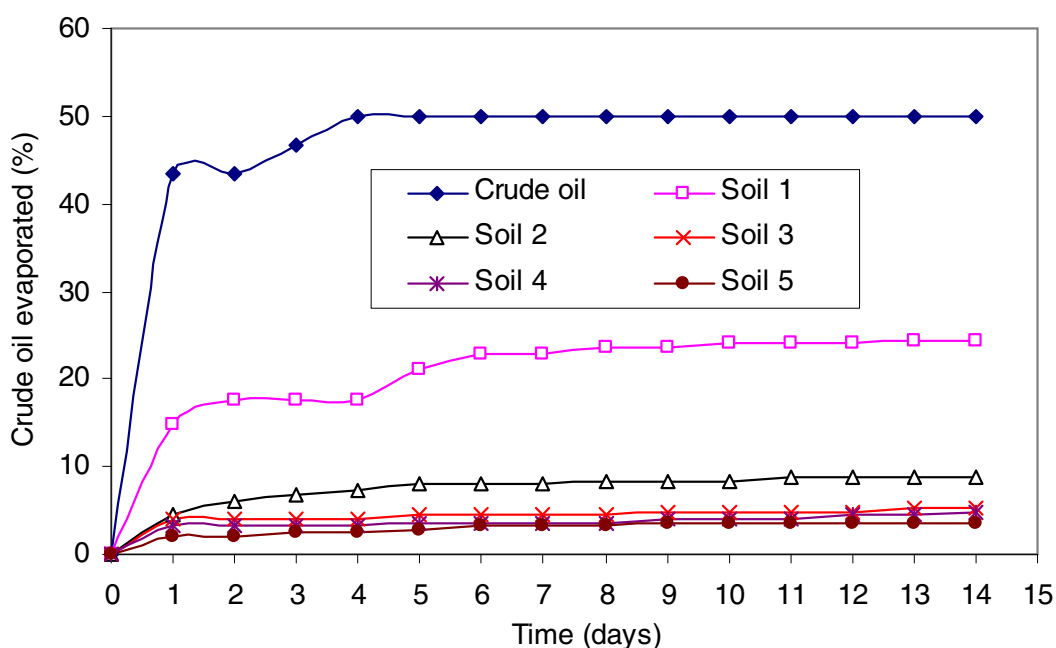


Figure 3.6. Crude oil evaporation from the contaminate soil samples.

Table 3.30. Initial mass of oil in the soil samples (g)

Time (day)	Crude oil	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
0	30	250	250	250	250	250
1	17	213	239	240	242	245
2	17	206	235	240	242	245
3	16	206	233	240	242	244
4	15	206	232	240	242	244
5	15	197	230	239	241	243
6	15	193	230	239	241	242
7	15	193	230	239	241	242
8	15	191	229	239	241	242
9	15	191	229	238	240	241
10	15	190	229	238	240	241
11	15	190	228	238	240	241
13	15	190	228	238	239	241
14	15	189	228	237	239	241
15	15	189	228	237	238	241

As the weathering process continues, the colour of the less volatile oil components remaining in the soil changes. Butt et al. (1986) pointed out that due to evaporation, the proportion of higher molecular weight components in the oil would increase, which resulted to a contaminated soil with a higher density and viscosity. It was assumed that the non-hydrocarbon components in the oil (sulphur, asphaltenes and metals) will concentrate more than in the original oil.

#### 3.1.4 Gas Chromatography/Mass Spectrometer

To ascertain the extent of evaporation of the lighter oil components and to evaluate which compounds were lost, a GC/MS analysis was conducted for the two contaminants (see Section 3.2.3).

- Fresh oil themselves
- Oil extracted from the non-weathered contaminated soil (Soil – 4)
- Oil extracted from the weathered contaminated soil (Soil – 4)

Figure 3.7a-c shows the GC profile of Ekofisk crude oil. Since GC profile are always normalised with the highest hydrocarbon peak, Figure 3.7a shows that hydrocarbon less than C<sub>9</sub> was reduced before the contamination process. Comparison of Figure 3.7a & b shows that there was a loss of hydrocarbons during the contamination process. The hydrocarbon peak in Figure 3.7b was normalized with C<sub>11</sub>. Thus, this confirms the disparity in the amount of crude oil in soil as shown in Table 3.29.

However, in comparison of Figure 3.7b for the non-weathered sample and Figure 3.7c for the weathered sample, it was found that carbon number less than C<sub>16</sub> were reduced and the peak now normalized with C<sub>17</sub>. This study agrees well with the work of Gray et al. (1988), where washed sharp sand was contaminated with Kuwait crude oil at a ratio of 47:1 (sand: oil) by weight. Their resulting contaminated soil after heating for 7 days at 60°C indicated that crude oil extracted from the weathered contaminated soil through analysis with GC/MS shows that most aliphatic smaller than C<sub>16</sub> were reduced to trace level.

In addition, the base of the chromatogram in Figure 3.7c was noticed to have risen, leading to the formation of the unresolved complex mixture (UCM) which are material that cannot be detected by the GC/MS. Thus, it was concluded that after weathering of the contaminated soil, the remaining oil in soil has high molecular mass. Therefore, due to the loss of the volatile components of oil in the soil as result of weathering, the remaining oil in the weathered soil samples will tend to adhere and bind more in the soil surfaces than in the non-weathered soil samples. The weathering effect may be a limiting factor in the oil removal process from soil during soil washing process.

For the heavy oil, similar results were found like those of the crude oil as indicated in Figure 3.8a-c. The GC traces were featured by dominance of UCM with very small amount of resolved peaks being detected in Figure 3.8c. Thus, with the UCM observed from the chromatogram, the heavy oil will have the tendency of being difficult to removed from soil when compared with crude oil with less UCM.

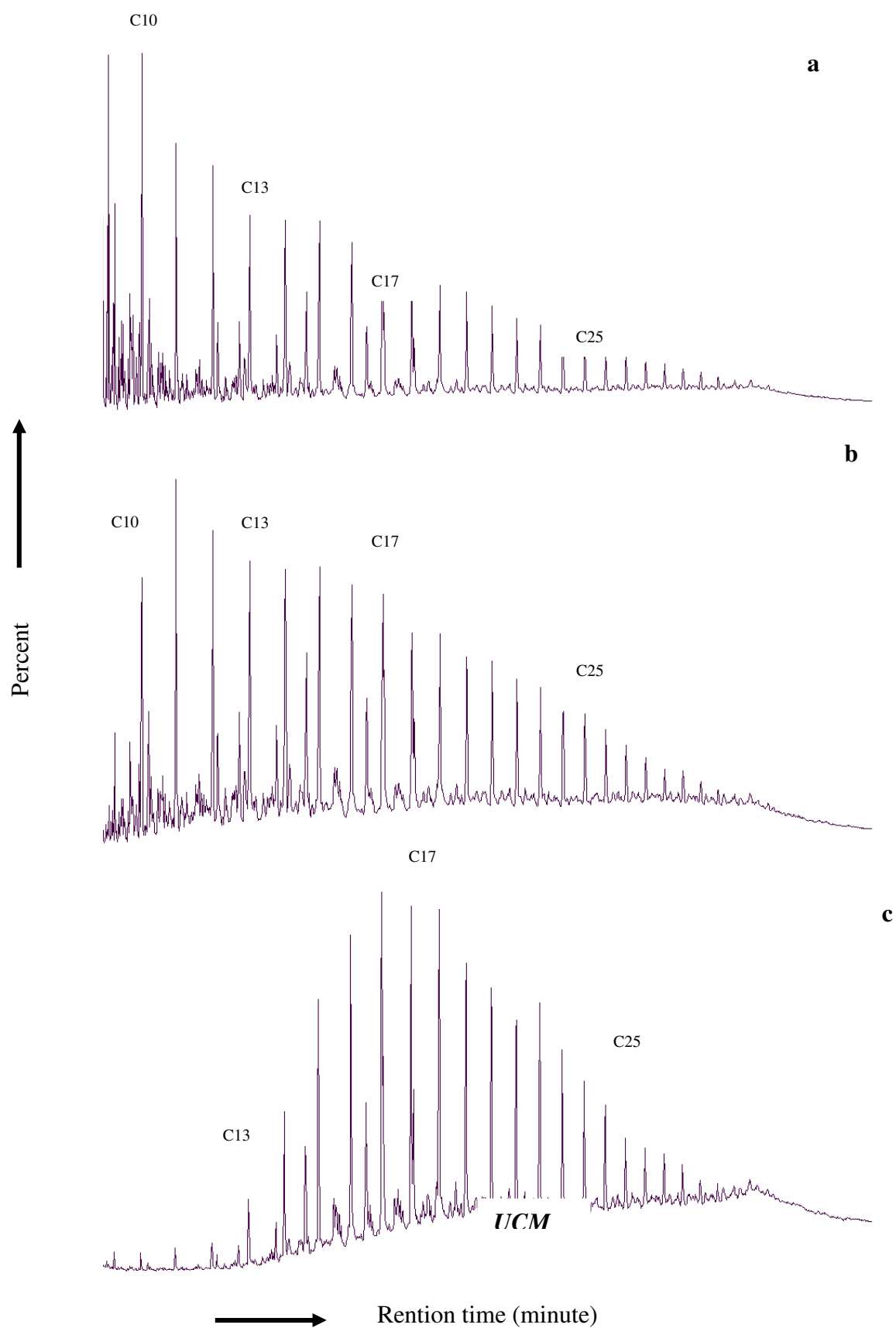


Figure 3.7. GC profile of Ekofisk crude oil: (a) fresh oil (b) non-weathered contaminated soil (c) weathered contaminated soil

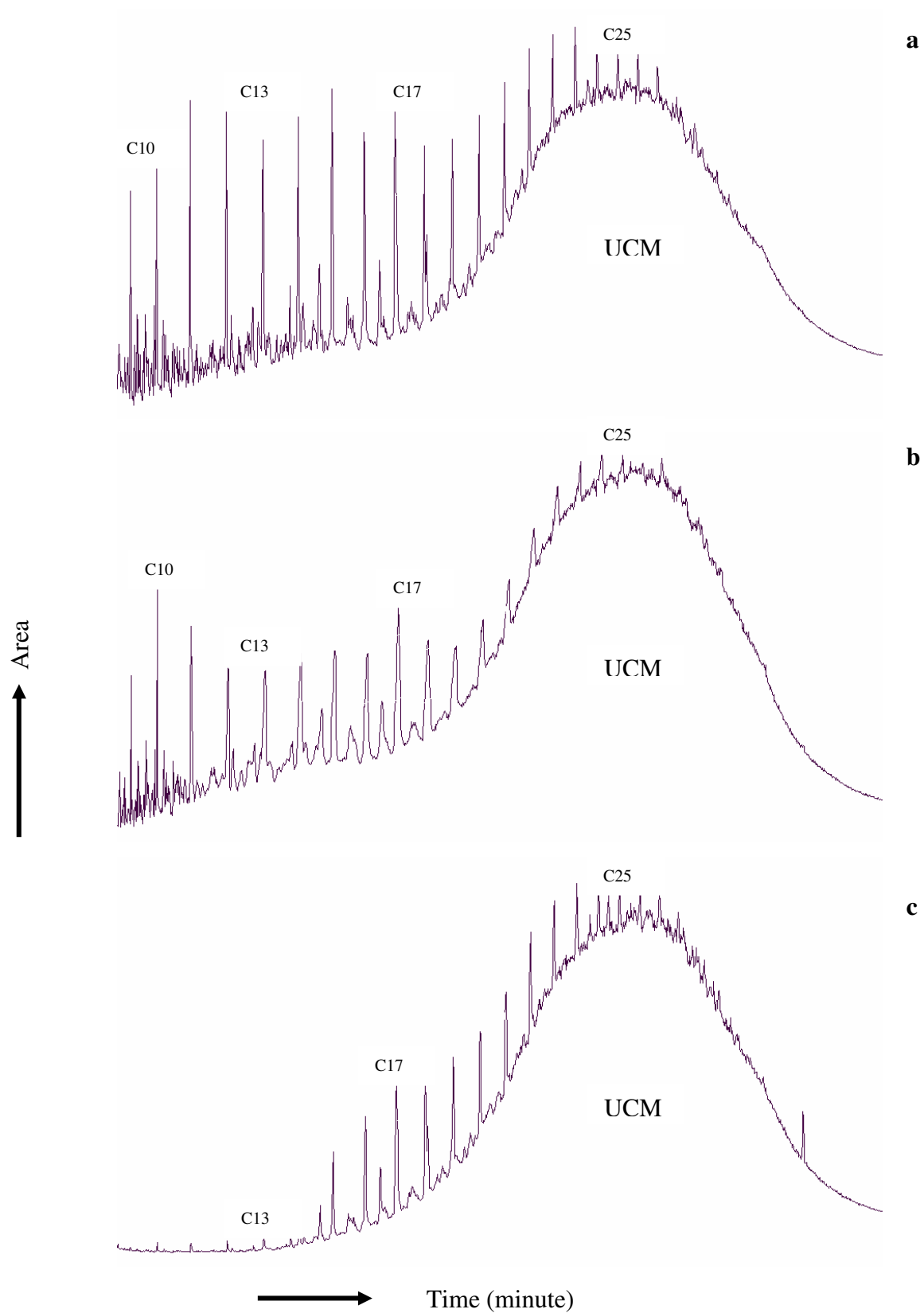


Figure 3.8. GC profile of heavy oil: (a) fresh oil (b) non-weathered contaminated soil (c) weathered contaminated soil

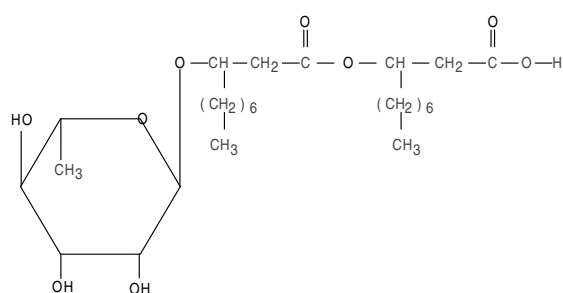
### 3.1.5 Surfactants

Several properties are used to characterize surfactant solutions. These characterizations will give an indication of surfactants' behaviour with either oil, soil or in combination of both or all of them. Characterizations herein are restricted to those properties that may affect the oil removal from soil with surfactants such as foaming, surface and interfacial tension, emulsion formation.

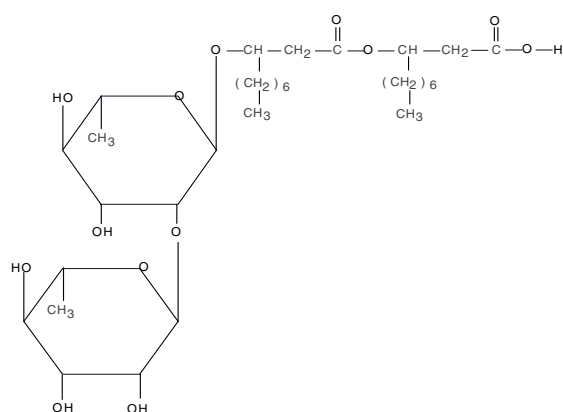
All the surfactants used and their chemical structures are presented in this section. The methods used in surfactant characterization are described in Section 3.2.4. Due to the novelty of the characterization study, the results were presented in Chapter 4 and were used to explain the soil washing process.

#### 3.1.5.1 Rhamnolipid

The rhamnolipid used is a blend of rhamnolipids RLL (R1) and RRLL (R2) that has been named by the manufacturer (Jeneil Biosurfactant Company, USA) as rhamnolipid JBR215 with 15 % active ingredients. Chemically, rhamnolipids are glycosides of rhamnose (6-deoxymannose) and  $\beta$ -hydroxydecanoic acid. The chemical structures of the rhamnolipid are presented in Figure 3.9.



RLL or R1 ( $\alpha$ -L-Rhamnopyranosyl- $\beta$ -hydroxydecanoyl- $\beta$ -hydroxydecanoate),  
 $C_{26}H_{48}O_9$  (504g/mole)



RRLL or R2 (2-O- $\alpha$ -L-Rhamnopyranosyl- $\alpha$ -L-rhamnopyranosyl- $\beta$ -hydroxydecanoyl- $\beta$ -hydroxydecanoate),  $C_{32}H_{58}O_{13}$  (650g/mole).

Figure 3.9. Chemical structures of rhamnolipids



### 3.1.5.2 Sodium dodecyl sulfate

Sodium dodecyl sulfate (SDS) is a synthetic anionic surfactant with purity of 97 %, supplied by Fluka Company, Switzerland. SDS used in this thesis has a chemical structure given in Figure 3.10.

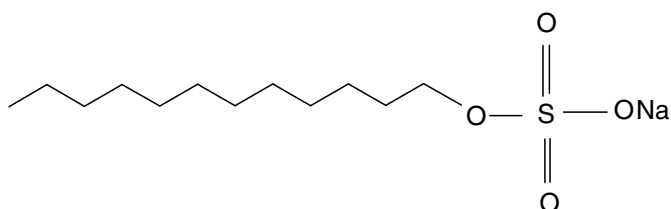


Figure 3.10. Chemical structure of SDS

### 3.1.5.3 Saponin

The saponin used throughout this study was a triterpene glycoside type from quillaja bark and contained  $\beta$ -D-glucuronic acid with carboxyl group of sugar moiety in hydrophilic fraction. Hong et al. (2002) argue that its elemental analysis shows 51% oxygen, 44% carbon, and 6% hydrogen. This material, with a purity of 10 %, was obtained from Sigma Chemical Co. USA and used without further purification. Its chemical structure is given in Figure 3.11.

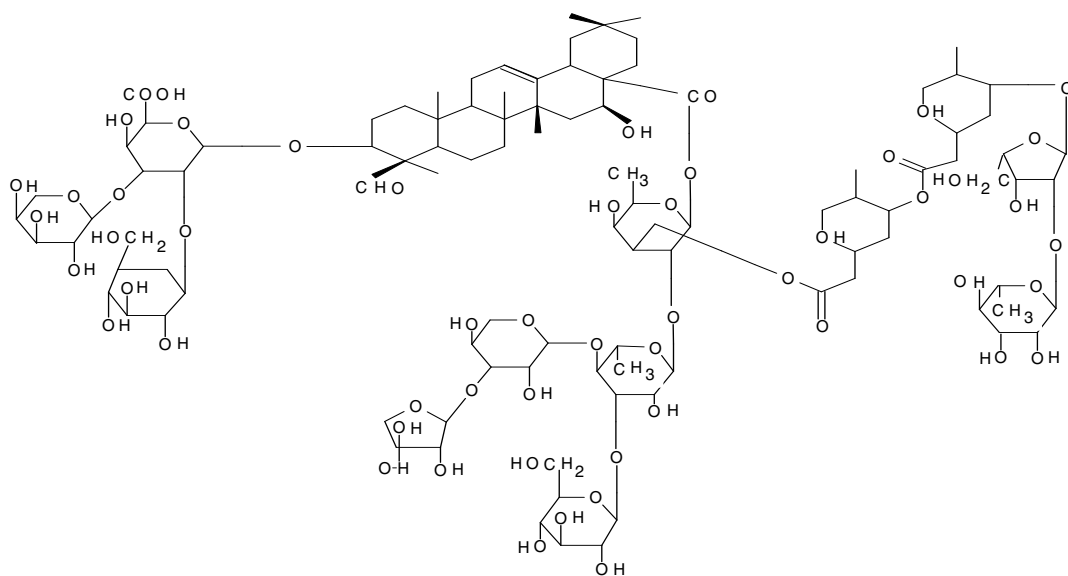


Figure 3.11. Chemical structure of saponin

#### 3.1.5.4 Aescin

Aescin (i.e.  $C_{54}H_{84}O_{23}$ ) or  $\beta$ -aescin has a purity of 90-95% and a molecular weight of 1101 g/mole, was supplied by Sigma Chemical Co, USA. It is one of the saponin preparations that are commercially produced from the seeds of the horse chestnut tree: *Aesculus hippocastanum* L. (Hippocatanacea) according to Pekdemir et al. (1999). This surfactant was used as supplied without further purification; its chemical structure representation is shown in Figure 3.12.

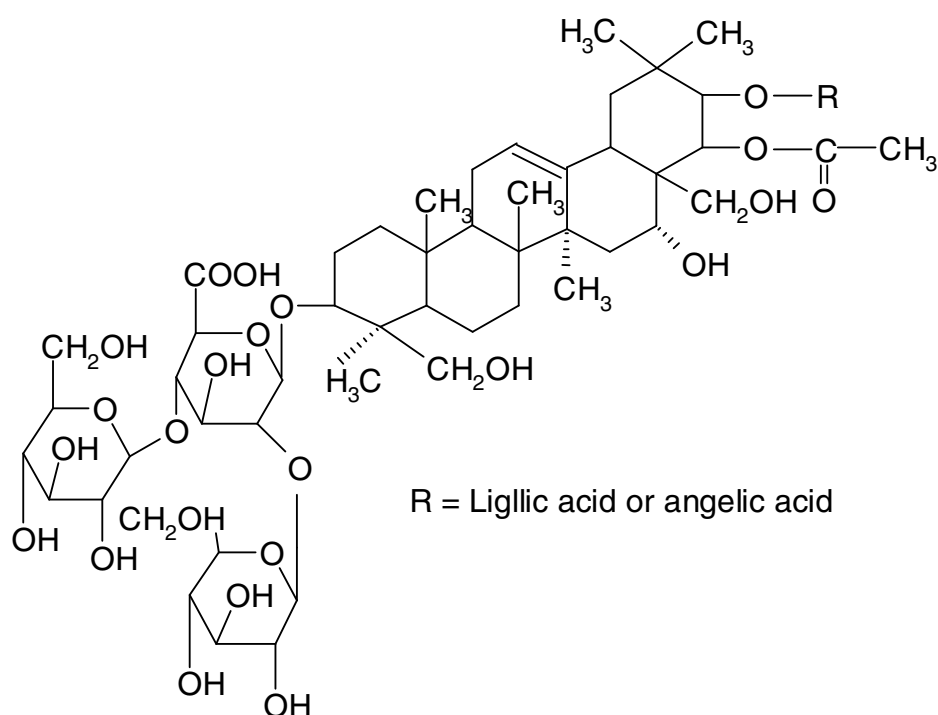


Figure 3.12. Chemical structure of aescin

#### 3.1.5.5 Tannin

Tannin (i.e.  $C_{76}H_{52}O_{46}$ ) of molecular weight 1701.22 g/mole and with purity of 90.8% was supplied by Fisher chemical, UK. The surfactant was used as supplied without further purification. The structure of tannin was not available within the literatures surveyed.

### 3.1.5.6 *Lecithin*

L- $\alpha$ -Phosphatidylcholine (L-  $\alpha$ -Lecithin) is derived from soybean. This Type II-S, was supplied by Sigma Chemical Co, USA. The product with a purity of about 19 % and chemical structure given in Figure 3.13 was used as supplied without further purification. In this study, this product was called Lecithin

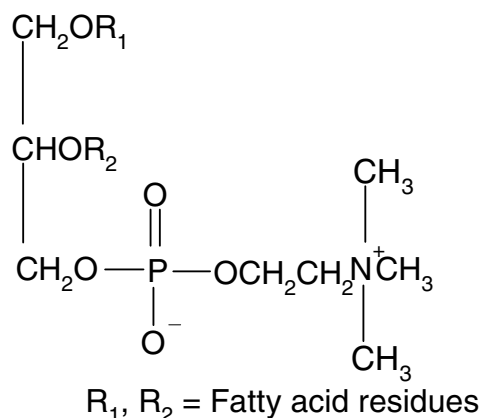


Figure 3.13. Chemical structure of lecithin

### 3.1.6 Salt

The chemical analysis of the TENNANTS PDV Salt –Food grade used to prepare seawater is shown in Table 3.31. This data was obtained from the supplier and indicated that the salt contains about 99.9 % sodium chloride.

The 3.5 %-mass seawater used throughout this study was prepared using 3.5g of the salt and made up to 100-  $\text{cm}^3$  in a volumetric flask with distilled water. Contents of the flask were shaken vigorously before use in further tests. In addition, the conductivity and pH were maintained as shown in Table 3.32.

# TENNANTS

## Technical Specification

### PDV Salt – Food Grade

Name and Formula	Sodium Chloride, NaCl
CAS No:	7647-14-5
EINCS No:	231-598-3
Appearance:	Crystalline White Product

#### TYPICAL CHEMICAL ANALYSIS

Components	Specification	
NaCl	99.9%	Codex Stan 150-1985
Ca	0.0005%	NEN 6426
Mg	0.00002%	NEN 6426
SO <sub>4</sub>	0.03%	NEN 6426

#### TYPICAL SCREEN ANALYSIS

> 0.6 mm	3.0%	DIN 66165
0.6 – 0.25 mm	92.0%	
0.25 – 0.125 mm	4.0%	
< 0.125 mm	1.0%	

Density: 1.2 – 1.3 g/cm<sup>3</sup>

Anticaking agent (E536) 8 (mg/kg) FAV 010

#### Odd and Harmful Components


All the demands for PDV salt food grade are followed at all times. The values of heavy metals are below the limit of detection.

AOX Aflatoxinen and pathogenic germs are not present.

Manufacturers Ref. TIS058/01/188


pdv fg

18-Sep-01



Responsible Care

Charles Tennant & Co. Ltd.  
Craighead, Whistleberry Road, Blantyre G72 0TH  
Tel: 01698 717900 Fax: 01698 717910



Certificate No. FS 11516  
of BS EN ISO 9002 1994

Table 3.32. Properties of seawater

Salt concentration	3.5 %-mass
pH @ 18.2 <sup>0</sup> C	8.28
Electric conductivity @ 20 <sup>0</sup> C	53 $\mu$ S/cm

### 3.1.7 n-hexane

The n-hexane used for the extraction of oil from contaminated soils was supplied by Fisher Chemicals, UK. The n-hexane has boiling point of 69°C, molecular formula (C<sub>6</sub>H<sub>14</sub>) and weight of 86.18g. Its elemental compositions are carbon (83.63%) and hydrogen (16.38%). Normal hexane is highly flammable, and its vapours can be explosive. Heat, sparks, and flames may ignite it. Flammable vapour may spread away from a spill. Also, it is incompatible with strong oxidisers and will react vigorously with oxidising materials such as liquid chlorine and concentrated oxygen.

### 3.1.8 Reagents used to determine soil cation exchange capacity

The sodium acetate tri-hydrate (CH<sub>3</sub>COONa.3H<sub>2</sub>O) used here is from BDH Laboratory Suppliers, England. FISON'S Scientific Equipment, England, supplied ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>) and ethanol (C<sub>2</sub>H<sub>5</sub>OH) with purity of 99.9% was supplied by Fisher Scientific, United Kingdom.

### 3.1.9 List of equipment used

The equipment used through out this project is listed in this section. More especially, those equipment used for the characterisation of surfactants, soils and oil. Then followed by the other ones used during the soil washing studies.

#### \* Apparatus and materials for measuring pH

A Model pH meter with a glass electrode, beakers, a precision measuring balance with readability of 0.005 g and distilled water.

#### \* Fan assisted oven

Supplied by Genlab Widnes, England: Operated between 5 and 200<sup>0</sup>C.

\* **Apparatus used for water content of soil**

Fan assisted oven maintained at temperature of 110 ± 5°C, measuring balance, containers for drying with the following dimensions: area 40 cm by 30 cm and height 2 cm.

\* **Sieving machine**

Manufactured by Endecott: test sieve shaker, England.

\* **Torsion tensiometer**

From white ELEC. INST. Co LTD; corrected at 20<sup>0</sup>C

\* **Visible spectrophotometer**

UV-HACH DR/2000 Direct reading spectrophotometer, Model 44800-00: Capable of reading within 361 to 998 nm wavelength.

\* **Temperature regulated water bath shaker**

Supplied by Grant instrument: with lateral shaker (10 to 200 stroke/minute) and temperature range of 5 to 100<sup>0</sup>C.

\* **Inductively coupled plasma**

Supplied by JOBIN YNON 138ULTRACE Emission Spectrometry. The Inductively Coupled Plasma (ICP) is an instrumental analysis technique that is based on atomic emission spectrometry. The quality of results obtained through ICP depends on the quality of the spectrometer used to analyse the light emitted by the atoms in the sample introduced into the touch. ICP can be used to measure all the stable elements in the periodic table with the exception of the gases. ICP requires no change in operating conditions between one element and another therefore it is a multi-elemental instrument.

\* **Centrifuge**

Supplied by MSE- Super minor centrifuge, England. The equipment was operated at 3000 rpm.

\* **Contaminating vessel for soil and oil**

Horizontally positioned drum mixer supplied by Grochopp & Co., Germany. Operated at 1400 rpm for one hour.

\* **Scanning Electron Microscope**

HITACHI S-2700 –Scanning Electron microscope, uses a software system called Princeton GammaTech and hardware – Sun Sparc 5 (UNIX) system.

\* **Pump**

WATSON MARLOW 505S peristaltic pump with up to 300cm<sup>3</sup>/minute flow rate

\* **Gas Chromatography/Mass Spectrometer (GC/MS)**

The GC/MS used was VG Quattro Tandem Mass Spectrometer (Waters, Manchester, England). Helium at flow rate of 1.5 cm<sup>3</sup>/minute was used as a carrier gas. Samples were injected on-column onto a 30m HP5 fused silica capillary column, 0.25mm i.d. (Agilent, England). .

\* **Mechanical stirrer**

Type RW20.n, supplied by IKA LABORATECHNIK, Taiwan (through CAMLAB).

## 3.2 Methods and procedures

### 3.2.1 Soil characterizations

Since not all the important properties of the soil samples were given by the suppliers, the soils were characterized in terms of their properties that are important for soil washing. The nature of soil's physical and chemical characteristics will determine how they contribute to the movement and retention of oil. These physio-chemical characteristics such as cation exchange capacity, porosity, surface area, particle size distribution and permeability will indicate the amount of oil that may be retained or sorbed by the soil, the soil-surfactant and the soil washing solutions interactions.

#### 3.2.1.1 Water content

ASTM Method D2216-98 ASTM (2003) which covers the laboratory determination of the water content of soils, rock and other similar materials was used in this study. The mass of the drying-container with dimensions (area 40 cm by 30 cm and height 2 cm) was measured and recorded, soil was then placed in the drying container and the mass of the container and the soil was measured. The soil and container were placed in the oven and drying was allowed for 24 hours to achieve a constant mass of soil at oven temperature of  $110 \pm 5^\circ\text{C}$ . After the 24 hours, the soil was allowed inside the oven to cool to room temperature ( $18^\circ\text{C}$ ), the mass of the dried soil sample and the container were then measured. The loss of mass due to drying is considered to be water in the soil pores. The water content was calculated by subtracting the mass of the dry soil sample from the original wet soil mass using.

$$w = \left[ \frac{M_{CWS} - M_{CS}}{M_{CS} - M_C} \right] \times 100 = \frac{M_w}{M_s} \times 100 \quad (3.3)$$

Where,  $M_C$  = Mass of container (g);  $M_{CWS}$  = Mass of container and wet soil (g);  $M_{CS}$  = Mass of container and oven dried soil (g)  $M_s$  = Mass of dry soil (g);  $M_w$  = Mass of water (g);  $w$  = Water content (%).



### 3.2.1.2 Particle size distribution

The Williams Sinclair Horticulture Limited soil after drying in the oven (Section 3.2.1.1) was sieved using Endecott test sieve shaker following the methods described by Head (1992) and Arora (1989) and the soil was classified into three different fractions. A total of 1000g mass of the oven dried soil was allowed to pass through the Endecott test sieve shaker with sieve sizes  $\leq 4$  mm. Mass of soil retained in each sieve was determined after shaking for 15 minutes. The percentage of soil retained in each sieve was determined using equation (3.2). The cumulative soil ( $P_n$ ) was calculated and values obtained were plotted in a graph against the soil particle sizes as shown in Figure 3.1. This study was repeated twice, with error range of  $\pm 0.05$  g.

$$P_n = \left[ \frac{M_n}{M} \right] \times 100 \quad (3.4)$$

Where,  $M_n$  is the mass of soil retained on sieve number  $n$  (g);  $M$  is the total mass of soil sample (g).

### 3.2.1.3 Porosity

A mass of 200 g oven-dried soil was emptied into a volumetric glass cylinder that resulted in a total volume of  $120 \text{ cm}^3$ .  $50 \text{ cm}^3$  of water was poured gradually into the glass cylinder that contained the soil samples. The process was stopped when the water level reached the top of the soil. At this level the soil reached saturation point and could not hold any more water. Figure 3.14 is used to illustrate the formation of different layers formed in the test.

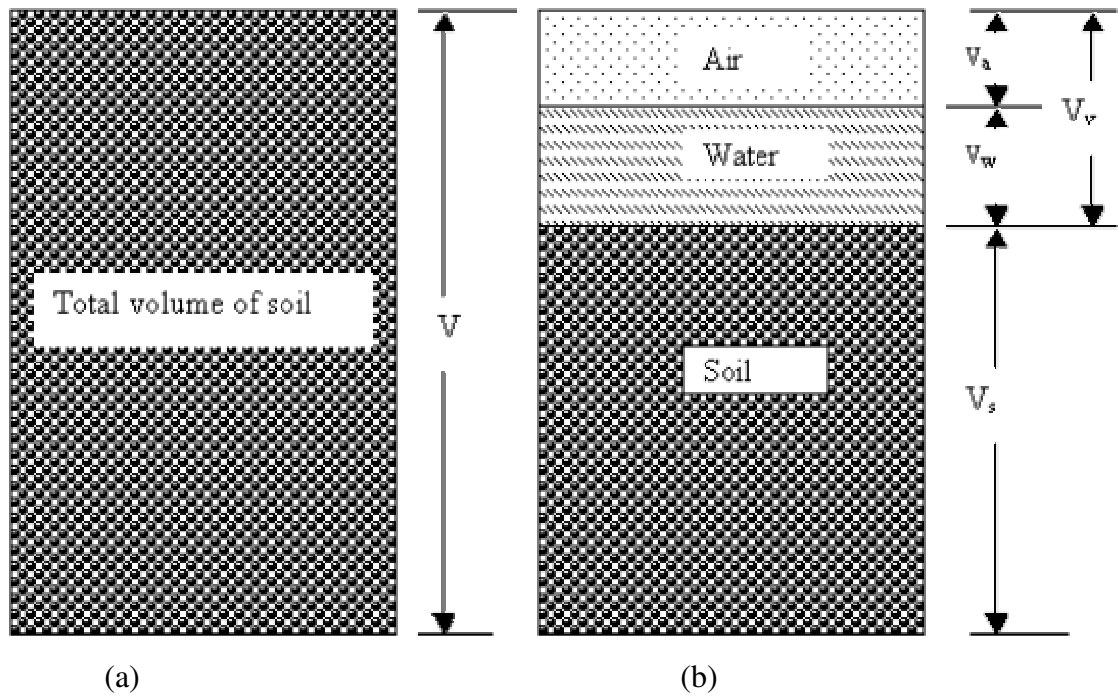


Figure 3.14. (a) soil existing in a natural state, (b) the different layers of soil after saturation with water.

The total volume of soil column in Figure 3.14 (b) can be expressed as:

$$V = V_s + V_v = V_s + (V_a + V_w) \quad (3.5)$$

Then,

$$\text{Porosity (n)} = \frac{V_v}{V} \quad (3.6)$$

$$\text{Void ratio (e)} = \frac{V_v}{V_s} \quad (3.7)$$

$$\text{Degree of saturation (S)} = \frac{V_w}{V_v} \quad (3.8)$$

Where,  $V$  is the total volume of soil.  $V_s$  is the volume of soil;  $V_v$ , volume of voids;  $V_w$ , volume of water;  $V_a$ , volume of air (which was assumed to be negligible);  $n$ , porosity and  $e$ , void ratio.

The relationship between porosity and void ratio is given by equation (3.9).

$$n = \frac{e}{1 + e} \quad (3.9)$$

While the relation between porosity, bulk density and soil density is shown in equation

(3.10).

$$Porosity(\%) = \left[ 1 - \frac{Bulkdensity}{Soil(particle)density} \right] \times 100 \quad (3.10)$$

#### **3.2.1.4 Bulk density**

A soil mass ( $M$ ) of 200g was taken from the oven dried soil sample and was poured in to a measuring cylinder and the resulting volume recorded. Thereafter, the soil bulk density ( $\text{g/cm}^3$ ) was calculated using:

$$Bulk\ density\ (g/cm^3) = \frac{\text{Mass of soil } (M)}{\text{Volume of soil } (V)} \quad (3.11)$$

Where  $M$  is the mass of oven-dried soil (g) and  $V$ , volume of soil ( $\text{cm}^3$ ). The study was repeated in triplicate with an error range of  $\pm 0.05 \text{ g/cm}^3$ .

#### **3.2.1.5 Permeability**

The constant head method described in Arora (1989) was chosen for this study since the soil particles have a high fluid conductivity due to the soil textural characteristics. Each test was conducted with 200 g of contaminated and clean soil that was filled in a glass column of internal diameter 4.0 cm that results in a height of 9.55 cm. The experimental set up is illustrated in Figure 3.15. The top and bottom of the soil column were fitted with a wire filter to prevent washing out of the soil particles, before the entire set up was clamped in a tripod stand.

Three different heads ( $h_y$ : 172.00 cm, 139.00 cm and 83.00 cm) causing flow of water through the soil samples was tested for the soil column stability. For each study, the head was kept constant and the outlet height ( $h_x$ ) of water was set at 44.00 cm. The coefficient of permeability ( $K$ ) was calculated using equation (3.12).

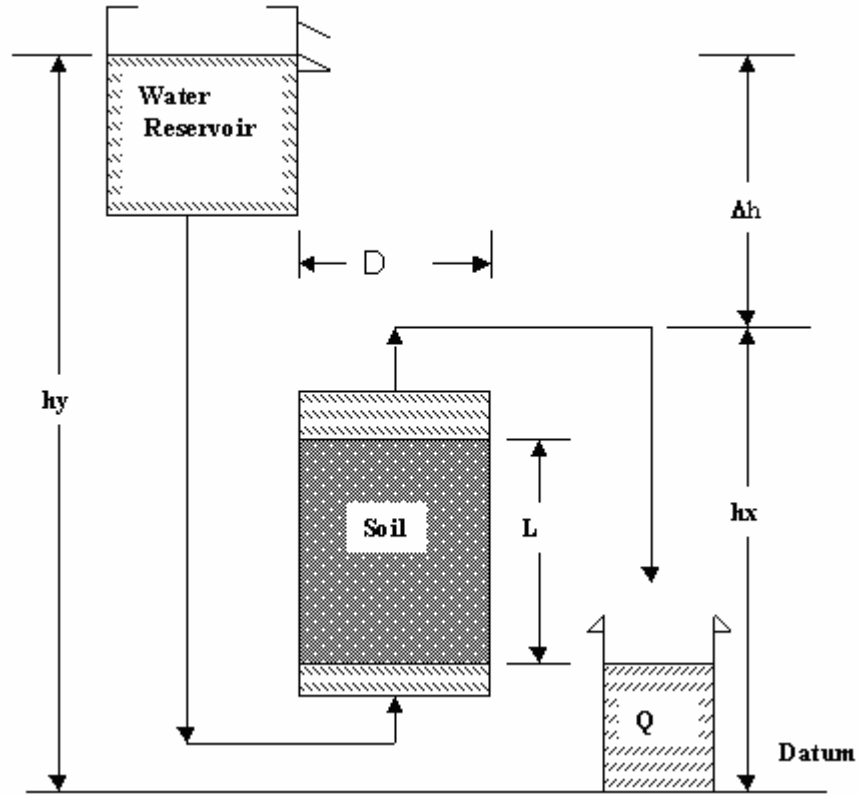


Figure 3.15. Schematic diagram used to study the permeability of soil.

The volume of water versus time values obtained after the outlet flow rate became constant was used to calculate the soil coefficient of permeability.

If,

$$K = \frac{VL}{A\Delta ht} = \frac{QL}{A\Delta h} \quad (3.12)$$

Then,

$$Q = KiA \quad (3.13)$$

Therefore,

$$i = \frac{\Delta h}{L} \quad (3.14)$$

and,

$$\Delta h = h_y - h_x \quad (3.15)$$

Where,  $K$  is the coefficient of permeability,  $i$  the hydraulic gradient;  $Q$  the volume of flow per unit time;  $V$  volume of water flowing through the soil at time  $t$ ;  $L$ , the length of soil through which flow occurs and  $A$  and  $D$  the cross sectional area and diameter of

the soil column respectively.

#### **3.2.1.6 pH**

The soil pH experiment in this thesis followed Method 9045 in USEPA (2003a) for the determination of soil and waste pH. This method is an electrometric procedure for measuring pH of soil and waste samples. Soil is mixed with water and the pH of the resulting aqueous solution is measured.

A mass of 20 g of each soil samples (Soil – 1, Soil – 2, Soil – 3, Soil – 4, and Soil – 5) was measured and poured in to 50 cm<sup>3</sup> beaker. Then 20 cm<sup>3</sup> of distilled water was added to the beaker, and the beaker was shaken laterally for 5 minutes. Thereafter, the beaker was allowed to stand for 1 hour so that most of the suspended materials could settle. pH measurement was taken in the beaker at 18.2<sup>0</sup>C.

#### **3.2.1.7 Cation exchange capacity**

Method 9081 in USEPA (2003b), being used for clay soil and non-clay soil was adopted for this study. The soil is mixed with sodium acetate solution, which results in the exchange of Na<sup>+</sup> in the sodium acetate to that in the soil. Thereafter, the soil is washed with ethanol followed by the addition of ammonium acetate solution to replace the absorbed sodium with ammonium. The concentration of the displaced sodium in ammonium acetate solution is then determined using Inductively Coupled Plasma (ICP).

### **Reagents preparations**

1N: Sodium acetate solution (NaOAc)

136 g of sodium acetate trihydrate (CH<sub>3</sub>COONa.3H<sub>2</sub>O) was dissolved in 950 cm<sup>3</sup> of distilled water. The pH of the solution was adjusted to 8.2 by adding acetic acid; thereafter the solution was made up to 1-litre with distilled water.

1N: Ammonium acetate solution (NH<sub>4</sub>Oac)

57 cm<sup>3</sup> of acetic acid (CH<sub>3</sub>COOH) was added to 800 cm<sup>3</sup> distilled water in a volumetric flask, then 68 cm<sup>3</sup> concentrated ammonium hydroxide (NH<sub>4</sub>OH) was added, the solution was mixed well and left to cool. The pH of the resulting solution was adjusted to 7.0 by adding acetic acid. The solution was then made

to 1 litre by adding distilled water.

Ethanol ( $C_2H_5OH$ ), 99.9%

### **Steps followed to determine CEC**

- Step 1: Due to the variations in soil particle sizes, 4g of Soil – 1 and Soil – 2, and 6 g of Soil – 3, Soil – 4, and Soil – 5 were weighed and poured into separate 45 cm<sup>3</sup> centrifuged test tubes.
- Step 2: 33-cm<sup>3</sup> of 1 N sodium acetate solution was added to the test tube and then shaken laterally in a temperature controlled water bath at 20<sup>0</sup>C for 5 minutes. Thereafter each test tube was centrifuged at 3000 rpm for 1-hour, and the supernatant was decanted and discarded. This was repeated three times.
- Step 3: 33 cm<sup>3</sup> of ethanol was used to wash the soil by shaking as in (Step 2) for 5 minutes. Each test tube was again centrifuged for about 1 hour so that the liquid was clear and the supernatant was decanted and discarded. Step 3 was repeated twice. As a check, the electrical conductivity (EC) of the third supernatant was less than 400  $\mu S/cm$ .
- Step 4: The adsorbed sodium from the soil was replaced by extracting with three 33 cm<sup>3</sup> portions of 1 N ammonium acetate solution. Each time the soil was shaken for 5 minutes and centrifuged for about 1 hour so that the supernatant liquid was clear. All the three resulting liquids were completely decanted into a 100 cm<sup>3</sup> volumetric flask. The volume of the liquid was brought to 100 cm<sup>3</sup> using 1N ammonium acetate solution.
- Step 5: A stock solution of ammonium acetate was prepared, and then diluted to different concentrations and a reading by ICP taken, which were used to draw a calibration curve.

ICP of the extract from the 100 cm<sup>3</sup> was measured and the concentration of sodium ion was calculated with the calibration curve. Hence, the CEC of each soil was calculated using the relations:

$$\text{CEC (meq/100g)} = \text{meq/L Na [calibration curve of (ICP)]} \times \frac{V_T}{M} \times \frac{100}{1000} \quad (3.16)$$

Where,  $V_T$  is the total volume of the extract ( $\text{cm}^3$ );  $M$ , the mass of soil (g)

### **3.2.2 Soils contamination with oils**

A fixed mass (2000g) of each soil fractions was measured and poured into a drum mixer. The crude oil blend or the heavy oil blend was used to contaminate the soils at  $20^\circ\text{C}$ . The amount of oil used per gram of soil samples was the same for each oil as given in Table 3.29. But the different amount of oil used for the different soil samples was due to the differences in soil properties such as particles size distribution and porosity, which may lead to oil drainage thus drainage of oil was minimized throughout the contamination process

#### **3.2.2.1 Contamination procedure**

The contamination process was carried out using a horizontally positioned drum mixer (Grochopp & Co. 4060 Viesen 1) at 1400rpm. The mixing lasted for one hour for each soil fraction. Thereafter, the contaminated soil samples were removed and stored in an airtight glass container to prevent evaporation of the lighter components before washing commenced. Due to the loss of oil and soil during the contamination process, the oil content in each soil was determined through n-hexane extraction (Section 3.2.6).

#### **3.2.2.2 Weathering of contaminated soils**

Samples from the contaminated soils (Section 3.2.2.1) were kept in a fan-assisted oven (Genlab Widnes) at  $50^\circ\text{C}$  for 14 days. The contaminated soils were poured in a tray with dimension of 30 cm by 40 cm following the approach used in Jokuty et al. (1995). Mass reduction of the contaminated soil was observed within the period of time. Thereafter, the amount of oil in each of the exposed soil samples was determined through n-hexane extraction method (Section 3.2.6).

### 3.2.3 Gas Chromatography/Mass Spectrometer

The Gas Chromatography/Mass Spectrometer (GC/MS) used was VG Quattro Tandem Mass Spectrometer (Waters, Manchester, England) with the following operating conditions: Electron impact ionisation, electron energy 70 eV, scan range 40 to 500 amu at 1 scan/second. Helium at flow rate of 1.5 cm<sup>3</sup>/minute was used as a carrier gas. Samples were injected on-column onto a 30m HP5 fused silica capillary column, 0.25mm i.d. (Agilent, England) and the temperature held at 55<sup>0</sup>C for 2 minutes, then increased from 55<sup>0</sup>C to 300<sup>0</sup>C @ 5<sup>0</sup>C/minutes thereafter, held at 300<sup>0</sup>C for 40 minutes. One micro-litre of the crude oil/n-hexane extract was injected into the equipment for each investigation.

### 3.2.4 Surfactants characterizations

As surfactants' behaviour is best described in aqueous solutions, it is of interest to mention here that all the surfactants were soluble in water for the purpose of this work. The surfactant solutions were prepared in standard 100 cm<sup>3</sup> volumetric flasks. Surfactants were measured on mass basis and emptied in the 100 cm<sup>3</sup> flask, then either distilled water or seawater was used to complete the solution to the graduated mark. After the preparation of the stock solution, it was diluted to obtain desired concentration using equation 3.17.

$$M_1V_1 = M_2V_2 \quad (3.17)$$

Where,  $M_1$  and  $V_1$  are the concentration and volume of the known solution while  $M_2$  and  $V_2$  are for the new solution to be prepared.

#### 3.2.4.1 Surface tension

The surface tensions of surfactant solutions (Section 3.1.5) were studied with Du Nouy tensiometer (TORSION BALANCE: TYPE 'OS') using a platinum ring method. The solutions concentration used was between 0.00001 and 10 %-mass. The surfactant CMC was determined by noting the concentrations at which the surface or interfacial tension first became minimum.



The torsion tensiometer was balanced at the zero mark then volumes of the surfactant at a particular concentration were poured into a concave dish and placed on the platform below the platinum ring. The platform with the concave dish was lowered and adjusted so that the surface of the surfactant was about 1 cm below the platinum ring. Thereafter, the platform was adjusted until the platinum ring came into contact with the surface of the surfactant. As the adjustment of the concave dish continued, the index pointer of the tensiometer was maintained at the zero reading until after a degree of movement that was independent upon the surface of the liquid. At this stage, the platinum ring suddenly departed from the surface of the surfactant and the value indicated on the tensiometer was the surface tension of the surfactant at the concentration tested. This experiment was conducted in triplicate at a temperature of  $17 \pm 4^{\circ}\text{C}$  and the average result reported as CMC of surfactant solution.

#### **3.2.4.2 *Interfacial tension***

An equal volume ratio of crude oil and surfactant solutions was poured into a glass beaker of diameter 4 cm and the resulting mixture used for the interfacial tension studies. The same procedure used in Section 3.2.4.1 was used for the interfacial tension study except that the balance of the tensiometer reading for zero was checked with the platinum ring completely immersed in the crude oil phase and not in the surface or the interface of crude oil-surfactant. The platinum ring was then completely immersed in the surfactant phase before the platform was gradually adjusted until a force necessary to detached the platinum ring upward from the surfactant-oil interface was exerted Jokuty et al. (1995). This experiment was repeated in triplicate at a temperature of  $17 \pm 4^{\circ}\text{C}$ .

#### **3.2.4.3 *Foaming***

This study was performed with a custom-built glass apparatus which is identical to that given in Figure 3.16 made following the dimensions given in ASTM (1992) that is identical to the Ross and Miles design in Rosen (1989). As water circulated through the receiver at  $50^{\circ}\text{C}$ , the surfactants solutions were allowed to fall from a height of 10 cm from the burette into the receiver containing the surfactant solutions. The surfactant solutions were prepared at different concentrations between 0.004 and 0.5%-mass. For

each surfactant at the different concentrations, the heights of foam formed in the receiver were measured immediately, and after five minutes. This study was carried out in duplicate and the results were reproducible at 8%.

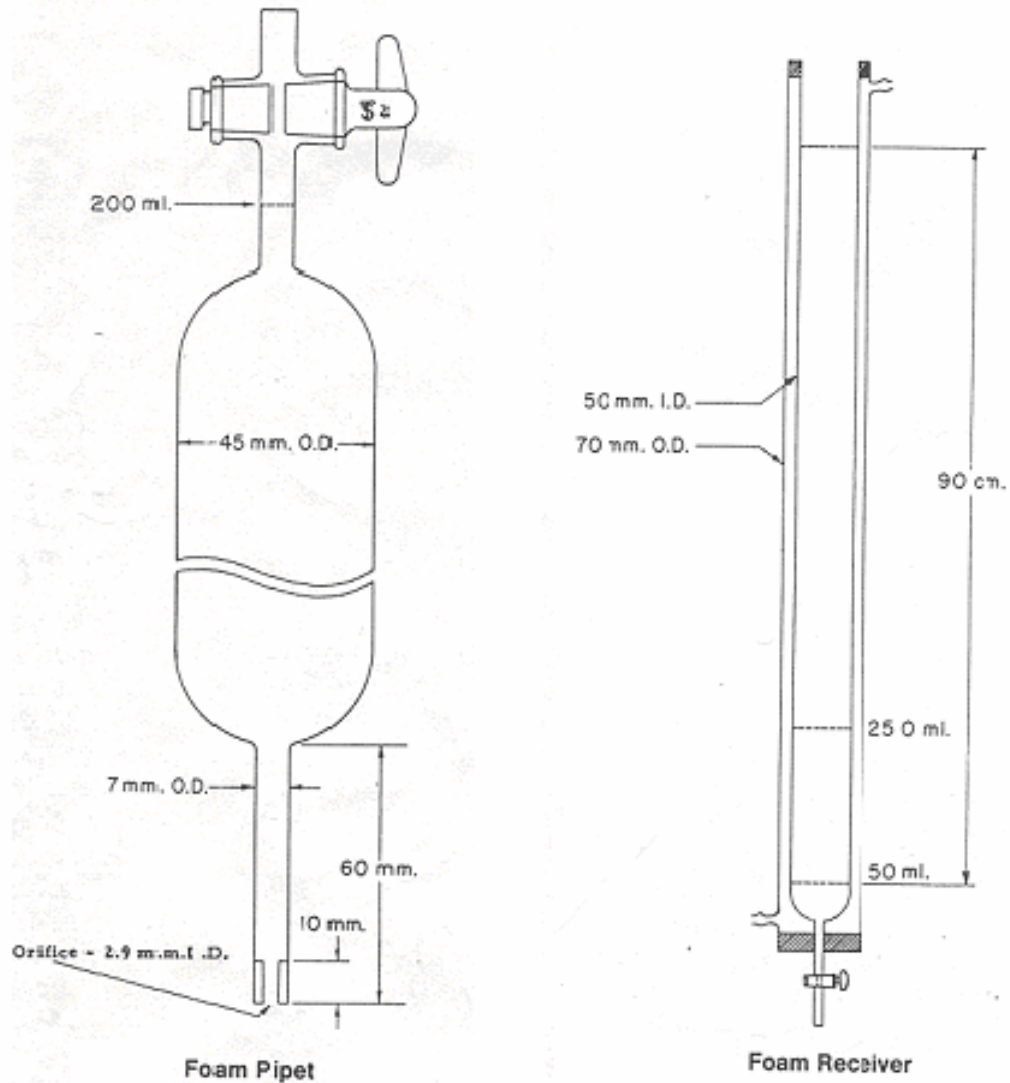


Figure 3.16. Apparatus for foaming study. Source from ASTM (1992)

#### 3.2.4.4 Sorption of surfactants

Surfactant sorption can be quantified for soils using surface-tension measurements. The surfactant-soil sorption approach in Chu and Chan (2003) was followed in this study. The study was carried out using a surfactant solution to soil ratio of 6:1 (volume/mass) in order to achieve an effective contact. The soil was placed in a 45 cm<sup>3</sup> centrifuge test tube and shaken laterally for 40 minutes. Thereafter, content of the test tube were

centrifuged at 3000 rpm for about 1 hour. The surface tension of the surfactant-soil supernatants was determined with Du Nouy tensiometer using a platinum ring method.

#### **3.2.4.5 Emulsion formation**

The surfactant solutions were prepared at varying concentrations between 0.05 and 5 %-mass. The efficiency of the solutions was determined for emulsion formation. The solutions were poured in test tubes with crude oil at different volume ratios of 7.5/2.5, 5/5, and 2.5/7.5 (surfactant solution/crude oil). The content in the test tube was shaken with a vibrating shaker at 1800 rpm for 2 minutes at constant temperature of  $18 \pm 2^{\circ}\text{C}$  and was then allowed to settle for 24 hours for phase separations and stability of emulsions. Thereafter, the volumes of the different phases were measured. The type of emulsion formed (o/w or w/o) was investigated by diluting 2 g of the emulsions in  $10\text{ cm}^3$  of either water or crude oil. The systems were shaken for about 30 seconds and allowed to settle for 5 minutes and the dilution of the emulsions in the different phases were observed. The electric conductivity of the emulsions was also determined using Corning Conductivity meter-200 at  $15^{\circ}\text{C}$ .

#### **3.2.4.6 Solubilization**

Saturated crude oil solutions were prepared by adding  $20\text{ cm}^3$  of Ekofisk crude oil to  $100\text{ cm}^3$  of the surfactants solutions prepared with distilled water or seawater into a  $250\text{-cm}^3$  separatory funnel. The contents in the funnel were shaken gently (200 strokes/minute) in a lateral shake with vertical displacement of 2.25 cm for 24 hours at room temperature of  $20\text{-}22^{\circ}\text{C}$ . According to Shiu et al. (1990), to avoid the formation of emulsions during the study, the shaking speed was kept constant throughout the study and the turbulence level of the liquids was maintained below that necessary to break off oil blocs from the oil layer. After the shaking, the contents of the funnel were allowed to settle for 48 hours and two separate phases formed (oil rich phase and surfactant rich phase). Next,  $25\text{ cm}^3$  of the surfactant rich phase was collected from the bottom of the funnel and analysis of oil in the surfactant rich phases was carried out by n-hexane extraction as follows:

The  $25\text{ cm}^3$  of the supernatant from the surfactant rich phase was poured into a  $45\text{ cm}^3$  centrifuge test tube with  $10\text{ cm}^3$  of n-hexane. The test tube was shaken laterally for

thirty minutes at 200 strokes/minute and contents was centrifuged for another thirty minutes to separate any suspended materials and to break any emulsion formed between the surfactant and n-hexane. As a check, a second extraction of crude oil remained in the supernatants were carried out; which always showed zero absorbance indicating no crude oil in the supernatant. The centrifuged supernatant was analysed for crude oil content using spectrophotometer at 400nm, the concentration of crude oil was then determined using the crude oil calibration curve (Section 3.2.6.1). The crude oil concentration in mg/liter was quantified and the solubilization ratio after the first extraction was determined by:

$$SR = \frac{S_C - S_{C,CMC}}{C_S - C_{S,CMC}} \quad (3.18)$$

Where  $S_C$  is the solubilization of crude oil at a given surfactant concentration ( $C_S$ ) and  $S_{C,CMC}$  is crude oil solubility at surfactant solution CMC ( $C_{S,CMC}$ ). The solubility was found to be reproducible to  $\pm 8 \%$ .

#### **3.2.4.7 Precipitation in seawater**

The precipitation study was investigated for rhamnolipid, SDS and saponin at the following concentrations: 0.004, 0.02, 0.1 and 0.5%-mass following the method described in Yin et al. (1995). 25 cm<sup>3</sup> of the surfactant solution in measuring cylinder was placed in a water bath at a temperature of 0°C with the aid of ice blocks. The height of the precipitate was noted and recorded, and volumes of precipitate formed were deduced every 1-hour interval for a total of 24 hours. With the surfactants' stock solutions, the absorbance of the unprecipitated solutions was measured with spectrophotometer at 300 nm and the concentration determined. This experiment was repeated in duplicate with a repeatability range of  $\pm 8\%$ .

#### **3.2.5 Soil washing methodology**

The descriptions of the different soil treatment methods (test tube, stirred tank, air sparging assisted stirred tank and vertical cylindrical column) tested are presented in this section. Each washing setting was developed based on the works reviewed in Section 2.4 and the materials characterized in Section 3.1. Due to this, each washing

setting has a unique washing conditions and characteristics such as volume of surfactant solutions that is needed to treat a certain mass of contaminated soil.

#### **3.2.5.1 *Test tube washing***

Five grams of the contaminated soils (Soil – 2, Soil – 3, Soil –4 and Soil – 5) samples were measured using OHAUS/TS400D - Precision standard balance and poured into 45-cm<sup>3</sup> centrifuged test-tube. A known volume and concentration of each surfactant solution was added to the contaminated soil in the test tube. The test tube was shaken laterally, with a horizontal displacement of about 2.25-cm, in a temperature regulated water bath shaker from Grant Instrument at different speeds (strokes/minute) under predetermined experimental conditions.

After each washing, the contents of the test tube (Soil – 2) were allowed to settle for 12 hours and about 3 minutes for Soil – 3, Soil – 4 and Soil - 5. The settling time applies to all washing settings and was chosen based on the soil particle size distribution in Arora (1989). The washed solution was decanted from the test tube after the defined settling time. The soil was then rinsed with 5 cm<sup>3</sup> of distilled water by lateral shaking for 3 minutes at the same washing conditions and the rinse water decanted after the appropriate particle settling time. The rinsing of the soil in the test tube was carried out to remove the oil from the walls of the test tube as well as the remaining surfactant solution from the soil. Another reason for the rinsing was to prevent the formation of an emulsion with the extracting solvent later when determining the remaining oil on the soils.

#### **3.2.5.2 *Effect of rinsing with water***

In order to investigate the effect of rinsing process on oil removal, oil remaining in the washed soil after a typical surfactant solution wash test was determined after using different volumes (1, 2, 3, 4 and 5 cm<sup>3</sup>) of water for rinsing. Oil remaining in soil was determined following the method described in Section 3.2.6 and the results are given in Figure 3.17. As seen from the figure, 4 cm<sup>3</sup> is sufficient to clean the oil smeared on the walls of the test tubes. Considering the removal of remaining surfactant solution in the washed sample and practically workable volume of rinsing water, it was decided to carry out rinsing using 5 cm<sup>3</sup> water.

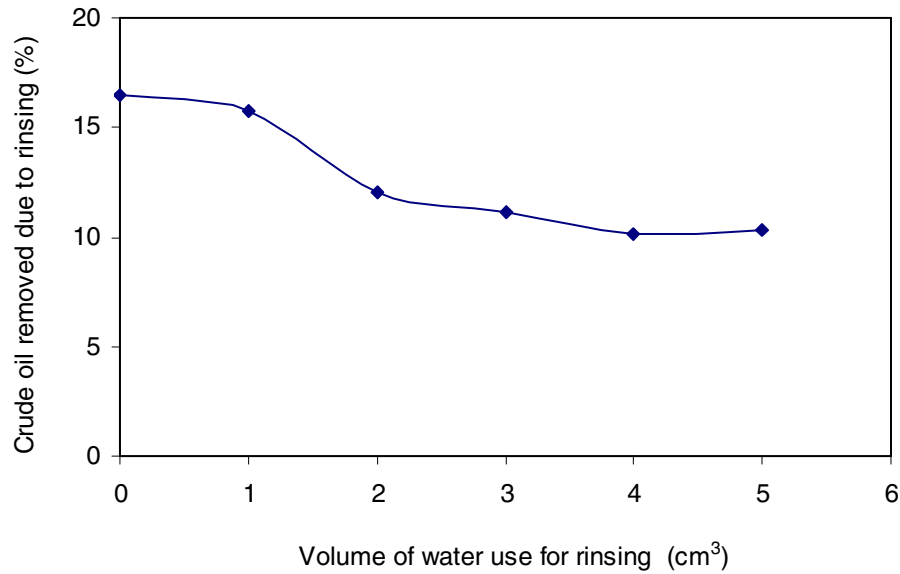


Figure 3.17. Effect of rinsing of washed soil

The contaminated soil contains about 998.80 mg of oil per 5 g of soil. Figure 3.17 showed that at zero cm<sup>3</sup> (no rinsing with distilled water after washing) about 16.48% of oil remained in the soil. However rinsing with 5 cm<sup>3</sup> water further reduced the oil in the soil to about 10.27%, indicating that rinsing water was able to remove about extra 5%. This is thought to be mainly due to the removal of oil stuck to the walls of the test tube.

### 3.2.5.3 Optimization method

The optimum conditions for washing soil were investigated using the Taguchi experimental design method. The explanation of the Taguchi method in Phadke (1989) is not discussed in this thesis, as it is not the main point of this study. However, the advantages of using the Taguchi method are:

- The experimental plan provides an economical way of simultaneously studying the effects of many parameters on process mean and variance.
- The Taguchi method is a fractional factorial design that can show process variability and stability.
- Most importantly, values determined at optimum conditions in the laboratory are reproducible in industrial application.

An Orthogonal array was chosen to determine the experimental plan,  $L_{16}(4^5)$  as shown in Table 3.33. According to Phadke (1989) and Peace Stuart (1995), this plan is most suitable for the conditions being investigated with five parameters and each with four levels as indicated in Table 3.34. The approach outlined in Section 3.2.5.1 was followed in washing Soil – 4 samples.

Table 3.33.  $L_{16}(4^5)$  Optimum condition investigation experimental plans

Experiment numbers	Experimental parameters and their levels				
	Temperature ( $^{\circ}\text{C}$ )	Conc. of solution (%-mass)	Vol. of solution ( $\text{cm}^3$ )	Shaking speed (strokes/min)	Time (minutes)
1	1	1	1	1	1
2	1	2	2	2	2
3	1	3	3	3	3
4	1	4	4	4	4
5	2	1	2	3	4
6	2	2	1	4	3
7	2	3	4	1	2
8	2	4	3	2	1
9	3	1	3	4	2
10	3	2	4	3	1
11	3	3	1	2	4
12	3	4	2	1	3
13	4	1	4	2	3
14	4	2	3	1	4
15	4	3	2	4	1
16	4	4	1	3	2

In order to observe the effect of noise source during the washing process, each experiment was repeated twice under the same given conditions at different times. The performance statistics was chosen as the optimization criterion, which was evaluated using equation 3.19 from Pignatiello (1988).

$$Z_b = -10 \log \left\{ \frac{1}{n} \sum_{i=1}^n \frac{1}{Y_i^2} \right\} \quad (3.19)$$

Where  $Z_b$  is the performance statistics,  $n$  the number of repetition done for an experimental combination and  $Y_i$  the performance value of the  $i^{th}$  experiment.

Table 3.34. Experimental parameter levels for test tube washing

Studies	Parameter levels tested			
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>
Washing temperature ( $^0\text{C}$ )	5	20	35	50
Volume of solutions ( $\text{cm}^3$ )	5	10	15	20
Conc. of solutions (%-mass)	0.004	0.02	0.1	0.5
Shaking speed (stroke/minute)	80	120	160	200
Washing time (minutes)	5	10	15	20

With the Taguchi method, the experiment corresponding to optimum working conditions might not have been carried out during the whole period of the experimental stage. In such cases the performance value corresponding to optimum working conditions can be predicted by utilizing the balanced characteristic of orthogonal array. For this purpose the additive model by Phadke et al. (1983) may be used as:

$$Y_i = \mu + X_i + e_i \quad (3.20)$$

Where  $\mu$  is the overall mean of the performance value,  $X_i$  the fixed effect of the parameter level combination used in the  $i^{th}$  experiment and  $e_i$  the random error in the  $i^{th}$  experiment.

Since Equation (3.20) is a point estimate, which is calculated by using experimental data in order to determine whether results of the confirmation experiments are meaningful or not, the confidence interval must be evaluated first. The confidence interval at a chosen error level may be calculated as given by Ross (1987) as:

$$Y_i \pm \left\{ F_{\alpha;1,DF_{MSe}} (MSe) \left( \frac{1+m}{N} + \frac{1}{n_i} \right) \right\}^{1/2} \quad (3.21)$$



$$R_i \equiv \left\{ F_{\alpha;1,DF_{MSe}} (MSe) \left( \frac{1+m}{N} + \frac{1}{n_i} \right) \right\}^{1/2} \quad (3.22)$$

Where,  $F$  is the value of the  $F$  table,  $\alpha$  the error level,  $DF_{MSe}$  the degree of freedom of mean square error,  $m$  the degree of freedom used in the prediction of  $Y_i$ ,  $N$  the number of total experiments, and  $n_i$  the number of repetitions in the confirmation experiment.

If experimental results are in percentage, before evaluating Equations (3.19) and (3.20), transformation of the percentage values should be applied first using the following equations. Values of interest are then later determined by carrying out reverse transformation by using the same equation as in Taguchi (1987).

$$\Omega(db) = -10 \log \left( \frac{1}{P} - 1 \right) \quad (3.23)$$

Where  $\Omega(db)$  is the decibel value of percentage value subject to  $\Omega$  transformation and  $P$  the percentage of the product obtained through experiment.

The order of experiment was obtained by inserting parameter values into the columns of orthogonal array,  $L_{16}4^5$  chosen as the experimental plan. However, the order of the experiments was made random in order to avoid noise source which had not been considered initially and could take place during an experiment and affect the result negatively. The validity of this study was checked by a confirmation experiment conducted at the optimum conditions. This value was compared with the predicted oil removal at the same conditions.

#### **3.2.5.4 Stirred tank washing**

A total mass (10g) of the contaminated soils from (Soil – 1, Soil – 3, Soil - 4, and Soil – 5) was weighed using the precision standard balance and emptied into a glass reactor of 7.2 cm of internal diameter and 12 cm vertical height. The reactor was placed in a temperature controlled water bath: the level of water in the bath was about 4 cm above the contents in the reactor. A mechanically operated stirrer with two blades that could operate with a speed range of 60 - 600 rpm was inserted inside the reactor. The blade was positioned vertically at about 2 mm above the bottom of the reactor. Each blade of

the stirrer had a vertical height of about 1.3 cm and lateral length of 2.85 cm. A lid was used to cover the contents in the reactor against the escape of materials through evaporation during the washing process.

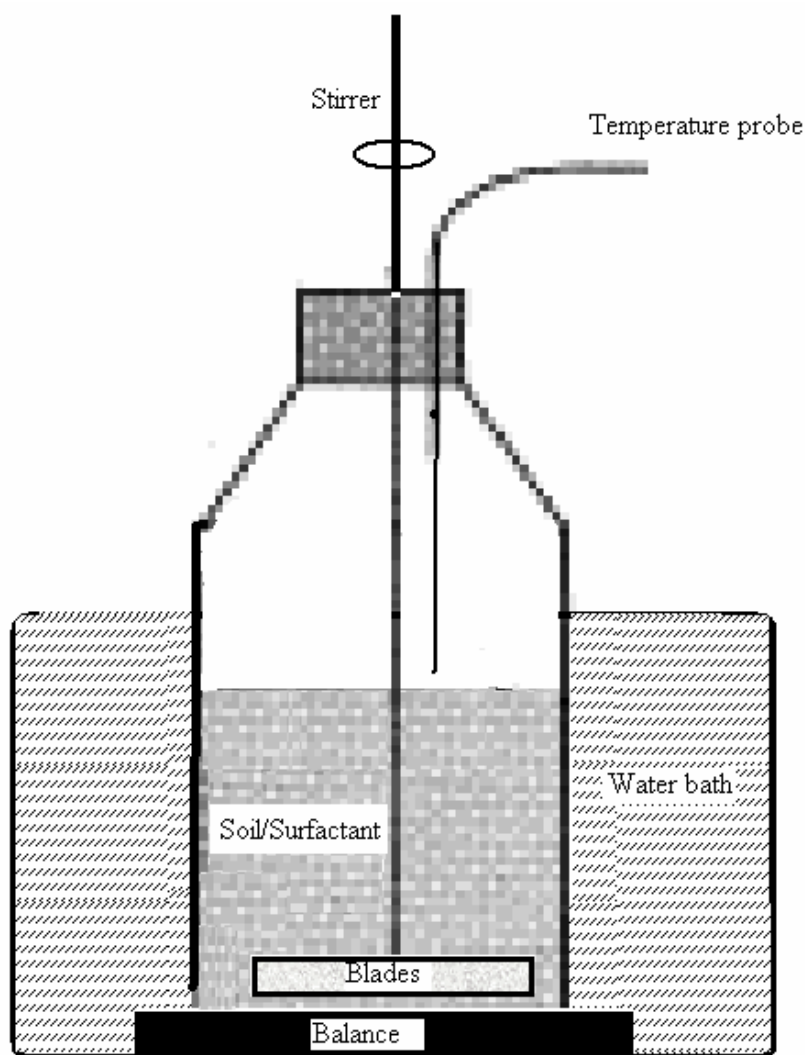


Figure 3.18. Schematic of the stirred tank reactor

After washing, contents of the reactor were allowed to settle for approximately 15 hours for Soil – 1 Arora (1989) and the other for 3 minutes, then the waste water decanted after the appropriate settling time was achieved. The washed soil was rinsed with 20 cm<sup>3</sup> of distilled water or seawater at the same washing conditions for 3 minutes and the wastewater decanted after the appropriate settling time of the soil was achieved. The rinsing of the soil was carried out to remove the oil that sticks to the walls of the reactor and to reduce the concentration of the surfactant solution that remained in the soil. This rinsing of the washed soil was also to prevent the possibility of emulsion formation between the surfactant and n-hexane during the extraction of oil remaining on soil later.

The effects of temperature, time, stirring rate, volume/mass ratios, and surfactant concentration were used to measure the efficiency of the surfactants' oil removal ability from the different soil samples following the experimental conditions in Table 3.35.

Table 3.35. Experimental parameters and levels for soil washing in stirred tank reactor

Studies	Parameter levels tested			
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>
Washing temperature ( <sup>0</sup> C)	5	20	35	50
Volume/mass ratio (cm <sup>3</sup> /g)	2	3	4	5
Conc. of solution (%-mass)	0.004	0.02	0.1	0.5
Washing time (minute)	1	5	10	15
Stirring speed (rpm)	240	360	480	600

#### 3.2.5.5 *Air sparging assisted stirred tank washing*

200 g of Soil – 4 was measured and poured in a custom-built stir tank reactor of internal diameter 12 cm and height 18 cm (Figure 3.19). The stirrer was maintained at a constant speed of 600 rpm, used for uniform distribution of the soil during washing. Compressed air at a pressure of 700 g/cm<sup>2</sup> ( $6.86 \times 10^4$  N/m<sup>2</sup>) was introduced through the frits at the bottom of the reactor. The reactor was then positioned vertically in a temperature controlled water bath. Thereafter, the experiment was conducted to study the removal of oil from soil with first distilled water and seawater, secondly with solutions of rhamnolipid, and SDS prepared with either distilled water or seawater.

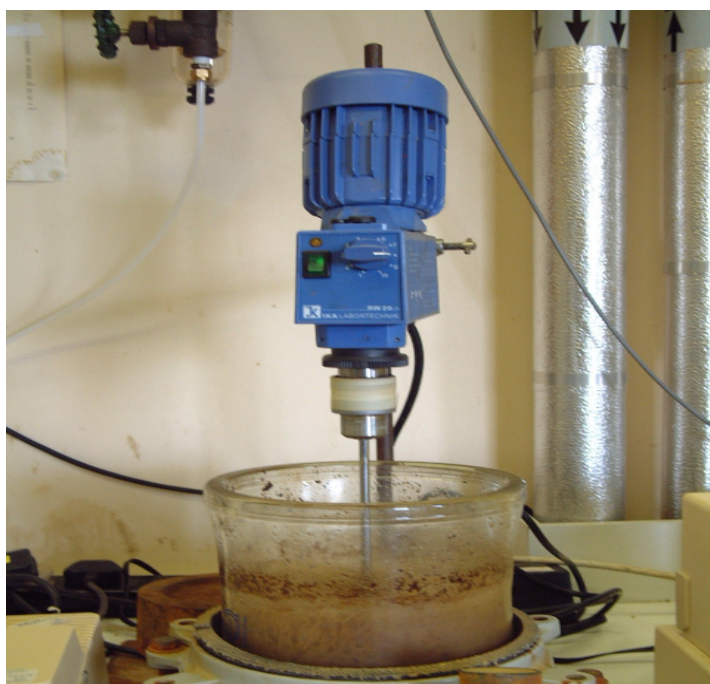


Figure 3.19. Picture of the air sparging assisted stirred tank reactor.

At each washing condition in Table 3.36, washing commenced and the effect of different parameters were observed. After the specified time of washing, waste water from the reactor was decanted and 200 cm<sup>3</sup> of either distilled or seawater (depending on the experiment) were used to rinse the washed soil for three minutes at the same washing conditions. The washed water was then decanted and the oil remaining in the soil was analysed.

Table 3.36. Experimental parameters and levels for soil washing in air sparging assisted stirred tank reactor

Studies	Parameter levels tested			
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>
Washing temperature (°C)	5	20	30	40
Volume/mass ratio (cm <sup>3</sup> /g)	15	25	35	45
Conc. of solution (%-mass)	0.004	0.02	0.1	0.5
Flotation time (minutes)	5	10	20	30

### 3.2.5.6 Column soil washing

The contaminated soil (200g) was packed vertically in a glass column that resulted in soil bulk density of  $1.64 \text{ g/cm}^3$ , soil column height of 9.55 cm with column internal diameter of 4 cm. The porosity of the soil column was 33.33%, giving a pore volume of  $40 \text{ cm}^3$  within the soil column. The inlet and outlet end of the column was fitted with wire filters to prevent the washing out of soil. The soil column was secured and fastened in a tripod stand as shown in Figure 3.20. The column was first filled with 0.5 PV (pore volume) of distilled water prior to the introduction of the contaminated soil. Another 1.5 PV of distilled water was pumped upwards through the soil column to remove all the air trapped in the soil column at a flow rate of  $2 \text{ cm}^3/\text{minute}$ .

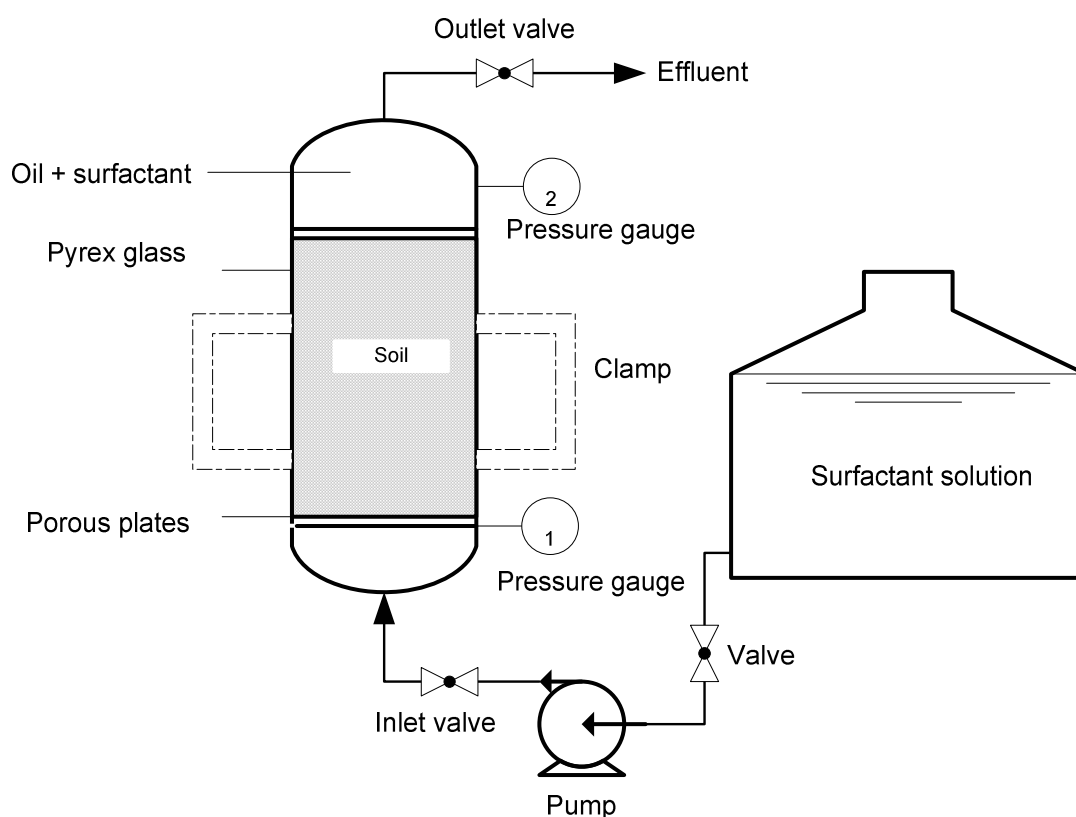


Figure 3.20. Glass column apparatus used in soil washing.

After removing the entrapped air and the soil column was fully saturated with distilled water, appropriate washing solutions were introduced into the soil column. The washing solutions used (distilled water and seawater, and solutions of rhamnolipid and SDS prepared with distilled water and seawater) were kept in a reservoir where they were pumped through the soil column against gravity.

To explain the experimental plans and parameter levels shown in Table 3.37, considering for instance during pore volume (PV) investigation for rhamnolipid solution, the following parameters were kept constant: concentration of surfactant 0.1%-mass, flow rate of solution 2 cm<sup>3</sup>/minute and washing temperature at 20<sup>0</sup>C. Then the PV was studied at 10, 30, 50, and 70. This approach was used for all the washing solutions.

Table 3.37. Experimental plan and conditions for column soil washing

Studies	Parameter levels			
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>
Pore volume	10	30	50	70
Conc. of solution (%-mass)	0.004	0.02	0.1	0.5
Flow rate (cm <sup>3</sup> /minute)	2	4	8	16
Washing temperature ( <sup>0</sup> C)	5	20	35	50

### 3.2.6 Analysis of oil in soils

Several analytical methods such as that of Eaton et al. (1995) have been proposed for quantifying the amount of oil in soil. Most of these methods use solvent such as chloroform in extracting the oil from soil. In analysing the extracts in the solvent, Ali et al. (1998) used UV-Visible spectrophotometer to quantify the amount of organics in sand. The result through these methods was assumed to be accurate as a calibration curve was set up. The extracted organics absorbed light at 260 and 410 nm. These two wavelengths were tested because most petroleum organic structures possessing double aromatic bonding absorbed at UV wavelengths while those that contain larger molecules absorbed at visible wavelength.

This research applied n-hexane as the extracting solvent throughout. The n-hexane is a

highly non-polar solvent and was chosen based on its availability and lower toxicity in comparisons with other solvents (such as the chlorofluorocarbons) listed in Sikdar and Irvine (1998). N-hexane was recommended as the extraction solvent for the determination of oil and grease and petroleum hydrocarbons in USEPA (1999) and has been used by Somasundaran et al. (1997), Zhang et al. (2001) and Zhang et al. (2001) to extract petroleum products from soil.

### 3.2.6.1 Calibration of oil

Stock solution of each oil was prepared in n-hexane. 1 gram of the oil was poured in a 100 cm<sup>3</sup> volumetric flask and made up to 100 cm<sup>3</sup> using n-hexane. The stock solutions were centrifuged for 20 minutes at 3000 rpm.

Using the stock solutions, the wavelength of the oil/n-hexane mixture was determined using a spectrophotometer. The absorbance of the stock solutions was measured at wavelength ranging from 390 to 450 nm. As indicated on Figure 3.21, 400 nm was observed to show the highest absorption of the light that passes through the solution, thus, was chosen for the entire study.

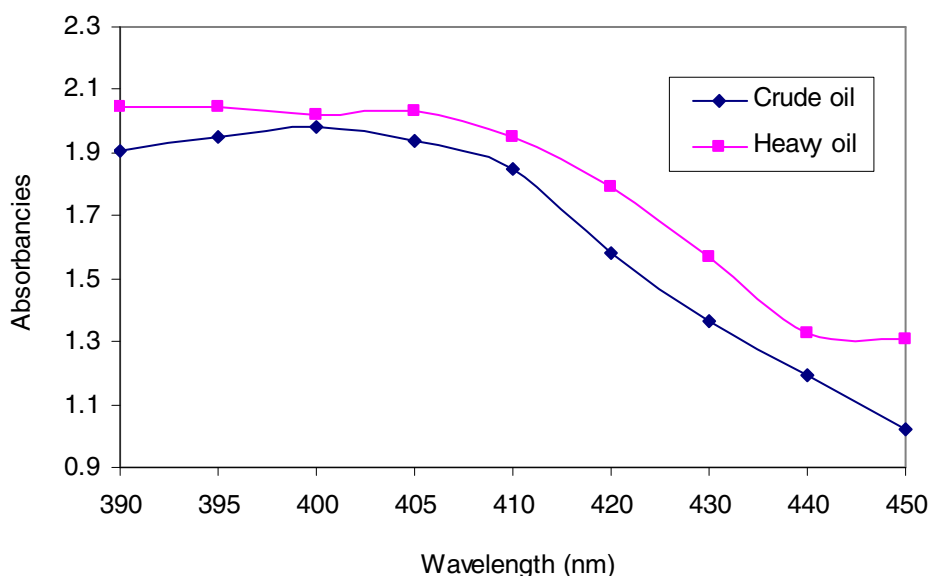


Figure 3.21. Determination of wavelength of the oil stocked solutions

A series of dilute solutions (20 ml) were prepared from the stock solutions and their absorbance measured at 400 nm. These were used to construct a calibration curve for each of the oil as shown in Figure 3.22.

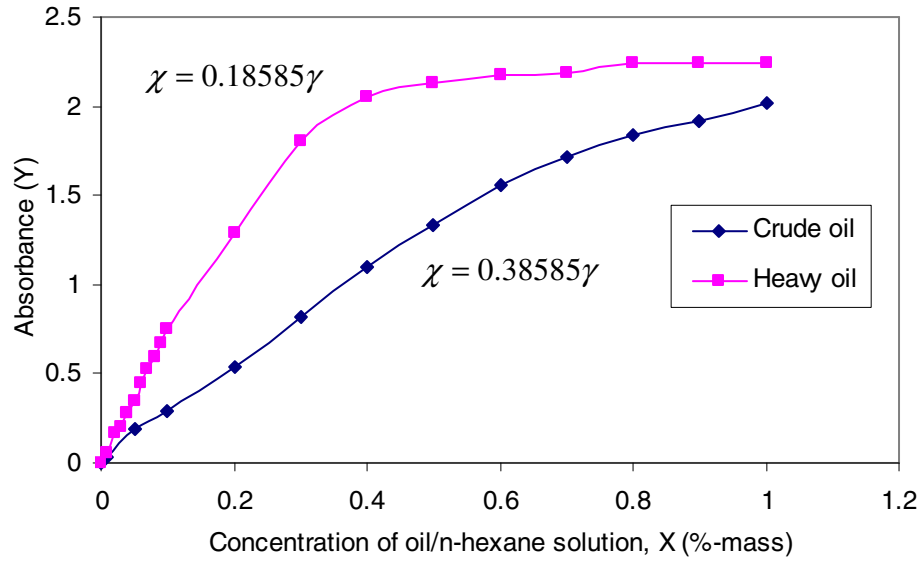


Figure 3.22. Calibration curves of crude and heavy oil at 20<sup>0</sup>C

The equations obtained after calibrating the two oils are given in equation 3.24 and 3.25. The equations were determined within the linear parts of the plots. This means that in measuring absorbance of oil remaining in soil, any value greater than 1.5 and 1.8 for crude oil and heavy oil was diluted and a new absorbance measurement taken.

$$\chi = 0.38585\gamma \quad (3.24)$$

$$\chi = 0.18585\gamma \quad (3.25)$$

Where  $\chi$  is the concentration of oil remaining in the washed soil (%-mass) and  $\gamma$  is the corresponding absorbance, measured at 400 nm.

### 3.2.6.2 Initial oil in soil before washing

Due to the loss of oil and soil through sticking on the mixing drum, during the contamination process, it was thought that the mass of oil in soil might be different from the amount added into the soil. Therefore, the amount of oil in soil was determined before the washing experiment using n-hexane was used for the extraction process. The concentration of the oil in the n-hexane extract was determined by measuring absorbance of the oil/n-hexane mixture at 400 nm and using the calibration curve produced above.



### ***3.2.6.3 Procedure to determine oil in soil***

Five grams of the contaminated soil were weighed and emptied into a 45 cm<sup>3</sup> test tube. 10 cm<sup>3</sup> of n-hexane was poured into the test tube and the contents in the test tube shaken laterally for 5 minutes. The oil/n-hexane extract was removed and the absorbance of the solution measured at 400 nm. Pure n-hexane was used as a control. This process was repeated again with another 10 cm<sup>3</sup> of n-hexane in the test tube containing the contaminated soil. The extract of the oil/n-hexane solution was also measured for absorbance. At the fourth 10 cm<sup>3</sup> extract, the absorbance reading was zero (the same as the control pure n-hexane) indicating nil presence of oil. The total extracted of oil/n-hexane solutions was collected together in a 50 cm<sup>3</sup> standard volumetric flask, and pure n-hexane was used to complete the solution to the graduated mark.

The sample from the 50 m cm<sup>3</sup> extract was centrifuged for about 20 minutes at a speed of 3000 rpm with a Centrifuge. This was done to separate any suspended particles in the n-hexane/oil solution and prevent interference with the absorbance readings. Absorbance of the centrifuged n-hexane/oil solution at 400 nm using the spectrophotometer was determined. Therefore, the concentration of oil at this absorbance was determined from the function obtained from the calibration curve of n-hexane/oil solution at 20<sup>0</sup>C.

### ***3.2.6.4 Procedure to determined oil removal***

Oil removal was determined based on the remaining oil in the soil following the washing. The remaining oil in the washed soil sample was extracted using n-hexane following the procedures in Section 3.2.6.3. After extracting the oil from the washed soil, the supernatant was centrifuged and the absorbance measured. The concentration of oil was determined using equations 3.24 and 3.25, and the amount of oil in soil deduced. In cases where the absorbance was not within the linear part of the oil/n-hexane calibration curve in Figure 3.22, the sample was diluted. This involved measuring 5 cm<sup>3</sup> of the oil/n-hexane solution and pouring into a 25 cm<sup>3</sup> volumetric flask. The content in the flask was completed to 25 cm<sup>3</sup> with n-hexane. Then, the absorbance of the new solution measured and the amount of oil remaining in soil calculated. The percentage amount of oil removed from soil was determined using the

equation below:

$$\text{Crude oil removed (\%)} = \frac{O_i - O_r}{O_i} \times 100 \quad (3.26)$$

Where  $O_i$  is the initial oil in the soil (g) before washing and  $O_r$  is the oil remaining in the soil (g) after washing.

For the test tubes and the stirred tank washing settings, the analysis to determine oil remaining in the soil was carried out immediately after rinsing in the reactors. However, for the column and air sparging study there were other processes involved. In the column test, after the appropriate washing was achieved, the soil column was unclamped from the tripod stand and the washed soil removed. Three layers of the washed soil were collected: 10g of washed soil samples from the top, middle and bottom of the column respectively. Each of these samples was emptied in a test tube and n-hexane was introduced into the tube to extract the oil from the soil following the method in Section 3.2.6.3. Results from the analysis indicated that oil remaining at the bottom and middle of the column showed not much difference (<3%). This was also applicable at the middle and top of the column. Thus, the average of these three layers was presented as oil removed from the soil column. For the air sparging assisted stirred tank washing, 10 grams of washed soil was collected from three different points of the equipment. Analysis also indicates that oil removal at the different parts had a difference less than 3%.

#### **3.2.6.5 Error and Repeatability**

The following steps were followed in error calculation: Repeating measurement several times and taking the average value:

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad (3.27)$$

Where n is the number of measurements, and  $x_i$  is the result of the  $i^{\text{th}}$  measurement.

Defining the variance  $s^2$  as:

$$s^2 = \frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2 \quad (3.28)$$

Then the standard deviation s as:

$$s = \sqrt{s^2} = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2} \quad (3.29)$$

Therefore, absolute error is given as:

$$\omega = \frac{x_i - \bar{x}}{\bar{x}} \times 100\% \quad (3.30)$$

Repeatability refers to the spread in results for the sets of independent trials of the same investigations or measurements. For example, repeatability in surface tension measurements may be affected by the ability to determine the exact location of the pointer on the tensiometer scale.

### 3.2.6.6 Absorbance theory

Generally, spectrophotometer measures the transmission of light through a substance. According to Harris (1997), when light is absorbed by a sample at a particular wavelength, the radiant power of the light beam passing through the sample will decrease. Therefore, the transmittance (T) is the fraction of the incident light that passes through the sample, which is given as:

$$T = \frac{P}{P_0} \quad (3.31)$$

Where  $P_0$  is the radiant power of the light beam that strikes the sample, and  $P$  is the radiant power that comes out in the other side of the sample. This radiant power is the energy per second per unit area of the light beam.

Transmittance has the range of values from 0 to 1. If no light is absorbed by the sample, transmittance is 1, if all the light is absorbed transmittance is zero. Percent transmittance (100T) also has value ranges from 0 to 100%. Thus, transmittance of 0.3 means that 0.7 (70%) of the light does not pass through the sample. Therefore, the less light is transmitted through a sample, the higher the absorbance.

Absorbance can be given as:

$$\gamma = \log \frac{P_0}{P} = -\log \frac{P}{P_0} = -\log T \quad (3.32)$$

Absorbance is proportional to concentration of light absorbing molecules in a sample as given by Beer's law:

$$\gamma = \chi \epsilon b \quad (3.33)$$

Where  $\epsilon$  is a constant called molar absorptivity and  $b$  is path length of sample (cm)

When no light is absorbed,  $P = P_0$  and  $\gamma = 0$ . If 90 % of the light is absorbed, 10% is transmitted and  $\gamma = 1$ . If 1% of the light is transmitted,  $\gamma = 2$ . If 0.1% of light is transmitted,  $\gamma = 3$ .

### 3.2.6.7 A typical oil removal calculation

5g of non-weathered crude oil contaminated soil sample (Soil – 4) was washed with 10 cm<sup>3</sup> of 0.1%-mass rhamnolipid solution for 20 minutes shaken at 200 stroke/minute at 20°C in test tube. Using n-hexane extraction, the initial crude oil in a similar 5g of contaminated soil sample was 0.60 g. The absorbance measurement of the washed soil sample after extraction with n-hexane was 1.897. This crude oil/n-hexane solution was diluted and new absorbance measure as 0.102. The dilute solution was prepared in a 20 cm<sup>3</sup> volumetric flask using 5 cm<sup>3</sup> of the original crude oil/n-hexane solution. The amount of crude oil remaining in the 5g-soil sample after washing was calculated as follows

From the calibration curve of crude oil, the corresponding value of concentration  $\chi$  is:

$$\begin{aligned} \chi &= 0.38585\gamma \\ &= 0.38585 \times 0.102 = 0.039\%-mass \end{aligned}$$

Thus, mass of oil remaining in 5g of contaminated soil sample would be

$$\begin{aligned} &= 0.039 \times 50/100 \times 20/5 \quad (20/5 \text{ is the dilution factor and } 50 \text{ is the} \\ &\quad \text{crude oil/n-hexane completed solution}) \\ &= 0.079 \text{ g} \end{aligned}$$

Therefore, oil removed from the 5g contaminated soil sample is

$$= 0.60 - 0.079 = 0.521 \text{ g}$$

The Performance (% of oil removed) of the biosurfactant solution is calculated as:

$$\begin{aligned} &= (\text{mass of oil removed}/\text{mass of initial oil in soil}) \times 100\% \\ &= (0.521/0.6) \times 100\% \\ &= 86.83\% \end{aligned}$$

### 3.3 Conclusions

The materials and the equipment used to characterize the soils, surfactants and oils have been studied, together with the methodology used in washing the contaminated soils. The conclusions drawn from this section includes the following:

#### *Oil characterization*

- The density and viscosity of the heavy oil ( $1.012 \text{ g/cm}^3$  and  $189.03 \times 10^{-2} \text{ cm}^2/\text{s}$ ) was greater than that of crude oil ( $0.835 \text{ g/cm}^3$  and  $10.14 \times 10^{-2} \text{ cm}^2/\text{s}$ ).

#### *Soil characterization*

- The soil water content of 0.54% for Soil – 4 was generalized for Soil – 3 and Soil – 5 because these soil samples are all derived from Soil –4 on dry wet basis through sieving.
- The soil water content will not influence the washing solutions performance in removing oil from soil by contributing to an increase in volume that may lead to the reduction of concentration of surfactant solutions and also water will not have any significant effect on extraction of oil from soil with n-hexane.
- More than 75% of the total soil mass was less than 2.00 mm in size, 15% between 2 – 4-mm and 10% was greater than 4.00-mm.
- The sieved soil with particle size less than 2.00-mm was classified as Soil –3, the next class (Soil – 4) was the entire soil mass that passed through the 4-mm sieve and the others with particle size between 2 - 4-mm was classified as Soil – 5.
- Texturally, Soil – 1 was considered as clay soil with more than 60% particles sizes  $\leq 0.002 \text{ mm}$ , Soil – 2 as silt soil with more than 60% particle sizes  $\leq 0.06 \text{ mm}$ , Soil – 3 as fine sand ( $\leq 2 \text{ mm}$ ), Soil – 4 as coarse sand ( $\leq 4 \text{ mm}$ ) and Soil – 5 as gravels (2-4 mm).
- The porosity of the contaminated soils shows the adverse affects of oil on soils' mechanical and physical properties. This can contribute to the reduction in permeability and poor aeration of soil due to the displacement of soil pores with oil. The soil porosity value was used to estimate the pore volume of surfactant during

soil washing in column setting.

- The soil bulk density of  $1.64 \text{ g/cm}^3$  could stand as a replica of a typical field sample likewise those of Soil – 3 and Soil –5.
- The coefficient of permeability obtained in this work was within the range of 0.01-1.00 cm/sec. This value was within the range the range given for coarse and medium sand, which is an indication that the soil permeability will control the mobility of surfactants or removed oil in soil during a soil column washing The flow of water in the column was stable, there was no air trapped in the soil column and settling or washing out of soil particles throughout the study.
- All the soil samples showed a neutral pH except Soil – 2 with pH of 6.29. The application of surfactant solutions during soil washing will not influence the acidity or alkalinity of soil samples. This will be advantageous for the soil washing studies since its main objective is to investigate the performances of the surfactant solutions at their natural properties such as pH.
- Knowledge of CEC will be useful in developing soil treatment procedures for different soils. This is because oil will tend to bind with soil that have greater amount of CEC.
- The pH of the surfactant solution is better to be within the pH of the soil, this approach will eliminate the possibility of accelerating CEC, if the pH of surfactant solution used is much greater.

#### *Contaminated soils*

- The soil contamination process shows that as the soil particle size increased less oil was needed to saturate the soil and the oil saturation with soil was limited to the quantity of oil that could withstand the total mass of soil without draining
- The disparity of oil initially used for contamination and those observed after the contamination are due to the loss of materials during the contamination process
- Through n-hexane extraction more than 97% of crude oil was removed from soil
- Through the process of weathering the volatile components of the oil were lost due to evaporation within the first 24 hours thereafter, the mass reduction of the contaminated soil was not changing
- As the weathering process continues the proportion of higher molecular weight components in the oil increase due to the concentration of components in the oil such as sulphur, asphaltenes and metals which result to a contaminated soil with a

higher density and viscosity

- The GC studies was used to show the disparity in oil
- It was found that carbon number less than  $C_{16}$  were lost and the peak now normalized with  $C_{17}$ .
- The base of the chromatogram was noticed to have risen leading to the formation of the unresolved complex mixture (UCM).
- The remaining oil in the weathered soil samples will tend to adhere and bind more in the soil surfaces than in the non-weathered soil samples. The weathering effect may be a limiting factor in the oil removal from soil during soil washing process.
- The GC traces were featured by dominance of UCM with very small amount of resolved peaks being detected
- The heavy oil will seems to be difficult to be removed from the soil when compared with the crude oil with less UCM in the weathered samples.

## 4 Results and discussions

While the previous chapter examined the characterization of soil and surfactants, and the soil washing methods, in this chapter all the results from the soil washing studies are given. As well as this, qualitative crude oil removal from Soil – 4 and GC/MS studies to investigate if there are preferences in crude oil complex components removal is presented. Finally, optimization conditions were determined using the Taguchi experimental design method. The water used for soil washing is distilled water unless otherwise stated as seawater.

### 4.1 Surfactants characterizations

Soil washing capacities of surfactants are direct function of their properties. The biosurfactants described in Section 3.1.5 have never been characterised in details with crude oil, therefore this contributes a major scientific data for industrial application of surfactant.

#### 4.1.1 Surface tension

The result of the surface tension measurement is shown in Figure 4.1 for distilled water prepared solutions. It indicated that the CMC of rhamnolipid (15%), aescin saponin, lecithin, tannin and SDS occur at solution concentrations of 0.02, 0.1, 0.1, 0.4, 0.008 and 0.2%-mass respectively. The solutions prepared with seawater have CMC at 0.05, 0.20, 0.20, 0.40, 0.01 and 0.20%-mass for rhamnolipid, aescin saponin, lecithin, tannin and SDS respectively. As certain factors such as temperature, electrolyte and water hardness affect the CMC of surfactants in aqueous solutions, the CMCs obtained here were compared with those that exist in the literature. CMC of various surfactants compares well with those available: for example, saponin with Hong et al. (2002), SDS with Holmberg (2002) and Deshpande et al. (1999) and aescin can be compared with that by Pekdemir et al. (1999). Therefore, the CMC of the other surfactants were assumed to be accurate. Surfactants' reduction of air-water surface tension indicates their ability to reduce the interfacial force that holds oil and soil together.



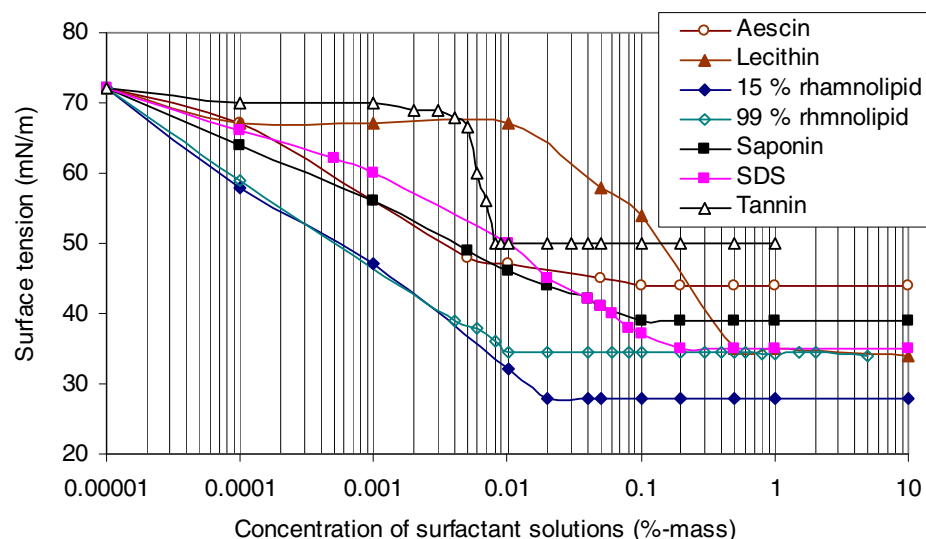


Figure 4.1. Surface tension of surfactant solutions

#### 4.1.2 Interfacial tension

The interfacial tension between crude oil and distilled water was measured as 25 mN/m. As the surfactant solutions were added into the water and the interfacial tension measured, it was observed that the forces at the oil-water interface were reduced as shown in Figure 4.2. The reductions of interfacial tension indicate the ability of surfactants to remove oil from soil. As the interfacial tension between oil and water is reduced, the capillary force holding the crude oil and soil is equally reduced. Therefore, this reduction will increase the contact angle and the reduction of the capillary force holding crude oil and soil together which results in the mobilization of oil.

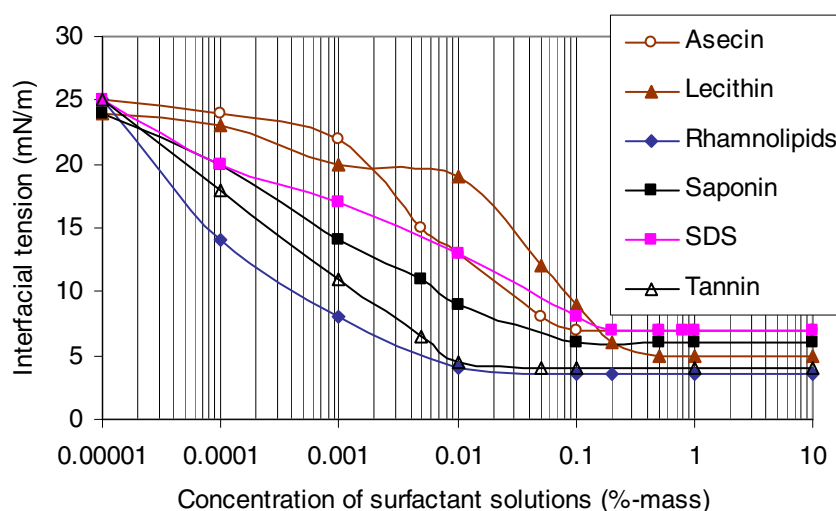


Figure 4.2. Interfacial tension of surfactant with crude oil

Since interfacial tension is concentration dependent, as aqueous solution concentration increases, the interfacial tension also reduces to the surfactant CMC value and remains constant. Figure 4.2 indicates that rhamnolipid and tannin would show more potential in oil removal from soil than the other surfactant solutions. This is because they have low CMC value that was able to reduce water interfacial tension to 4.5 mN/m. However, lecithin shows less potential in comparison with the other biosurfactants.

#### 4.1.2.1 Efficiency and effectiveness

The efficiency ( $\nu$ ) and effectiveness ( $\psi$ ) (Rosen (1989) and Elvers et al. (1994)) of the surfactant were determined by defining efficiencies as the bulk phase concentration of surfactant necessary to reduce the surface and interfacial tension to 55 and 7.5 mN/m respectively and the effectiveness as the maximal reduction in surface or interfacial tension obtained by addition of any amount of surfactant solution beyond CMC. In this case, this concentration is the same as the CMC value. Table 4.1 summarizes the values of  $\psi$  and  $\nu$ . The low efficiency of rhamnolipid at 0.0002%-mass will be advantageous for the treatment of oil contaminated media compared to that of lecithin which shows a concentration of about 0.08 %-mass in reducing the surface and interfacial tension of crude oil.

Table 4.1. Efficiency and effectiveness of surfactants

Surfactants	CMC (%-mass)	$\nu$ (%-mass)		$\psi$ @ CMC (mN/m)	
		@ 55 mN/m	@ 7.5 mN/m	ST	IFT
Aescin	0.1	0.001	0.06	44	7.0
Lecithin	0.4	0.08	0.15	35	5.0
Rhamnolipid	0.02	0.0002	0.0015	28	4.5
Saponin	0.1	0.001	0.03	39	6.0
SDS	0.2	0.003	0.15	35	7.0
Tannin	0.008	0.007	0.004	50	4.5

Where St is surface tension and ITF is interfacial tension

### 4.1.3 Foaming

The results of the forming test are given in Figure 4.3 and Table 4.2. It is seen from the figure that saponin has greater initial foaming ability than other surfactants. But saponin foams was not as stable as that of SDS and after 5 minutes saponin foams were less than those of SDS. SDS foaming was more stable over the tested range of concentrations, followed by aescin and then saponin. This result agrees with Lake (1989), that anionic surfactants have more stability than the non-ionic surfactants. Surfactants that show foam stability have a good detergency, which is the property of surfactant that shows their effectiveness in removing oil from a media.

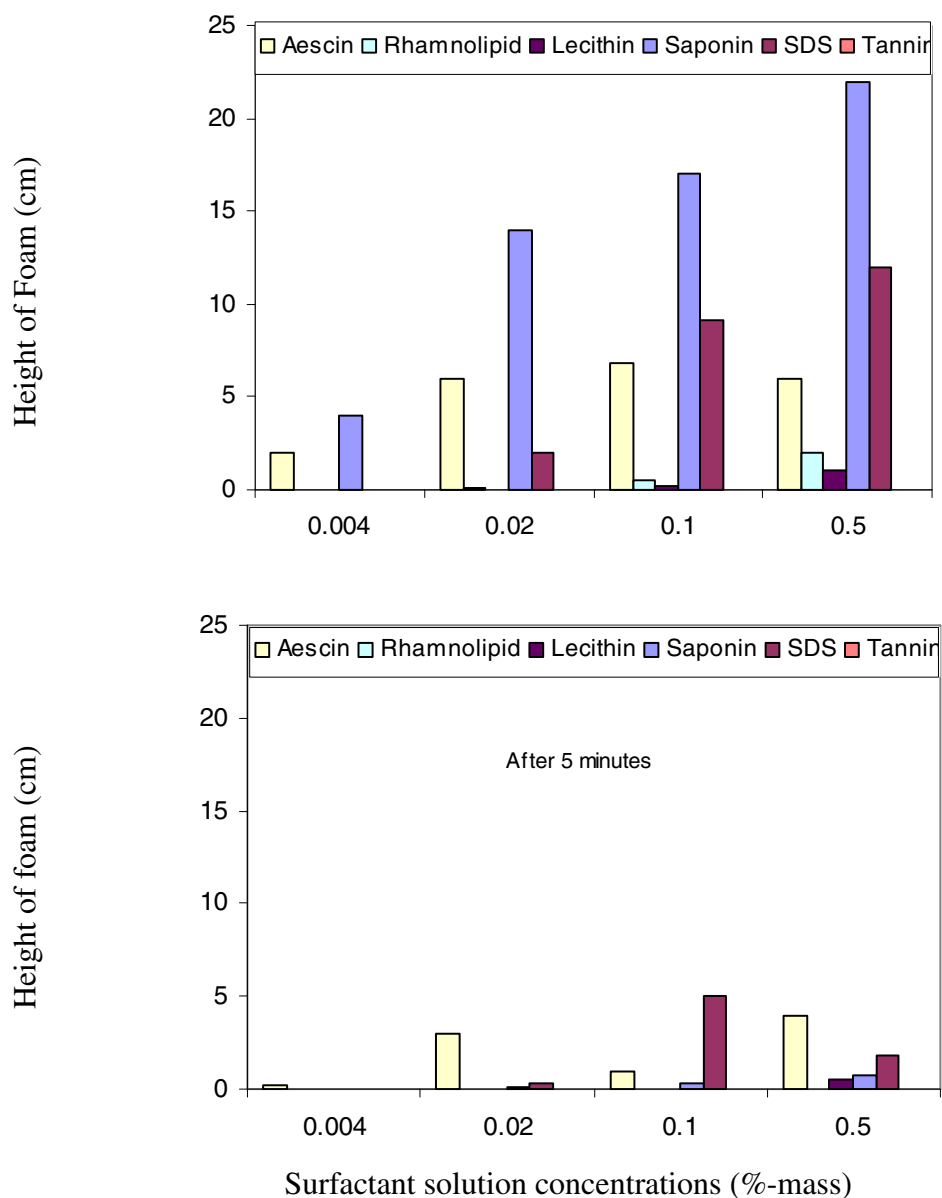


Figure 4.3. Foaming of surfactant solutions

Gravitational force was noted to be the main driving force for drainage, and can act directly on the film and indirectly through capillary suction in the Plateau borders, but can be opposed by the surface tension gradient along the air-liquid interface. The drainage rate of foams may be decreased by increasing the bulk viscosity of the liquid from which the foam is prepared. This may be achieved in aqueous systems by simply adding a solute with molecular weight greater than the aqueous phase. An alternative method to decrease the foam drainage kinetics is by increasing the surface viscosity and surface elasticity by packing a high concentration of surfactant or particles in the surface causing high adhesive or cohesive bonding.

Table 4.2. Surfactants foam heights

Solution conc. (%- mass)	Aescin		Lecithin		Rhamnolipid		Saponin		SDS		Tannin	
	I	A	I	A	I	A	I	A	I	A	I	A
	(cm)	(cm)	(cm)	(cm)	(cm)	(cm)	(cm)	(cm)	(cm)	(cm)	(cm)	(cm)
0.004	2	0.2	0	0	0	0	4	0.05	0	0	0	0
0.02	6	3	0	0	0.1	0	14	0.15	2	0.3	0	0
0.1	6.8	1	0.2	0	0.5	0	17	0.3	9.1	5	0	0
0.5	6	4	1	0.5	2	0	22	0.8	12	1.8	0	0

Where I is the initial foam height (cm) and A is the foam height after 5 minutes

#### 4.1.4 Sorption of surfactants

The surfactant sorption on soil was determined through measuring the surface tension of surfactant solution as prepared (fresh) and after being recovered at the end of soil adsorption test for a series of varying concentration of solutions. The two measurements were plotted together on the basis of the fresh solution concentration and CMC for the two cases were determined. As seen for a typical surfactant in Figure 4.4 as the fresh surfactant solution monomer reaches the CMC, it was assumed that the surfactant/soil supernatant would reach the CMC at the same monomers indicating the same surface tension at the CMCs. Therefore the difference between the CMC of fresh surfactant solutions and the CMC of the soil/surfactants supernatant indicates the amount of surfactant loss in the soil sample. Figure 4.4 to Figure 4.12 shows the plot of the fresh surfactant and soil/surfactant solutions.

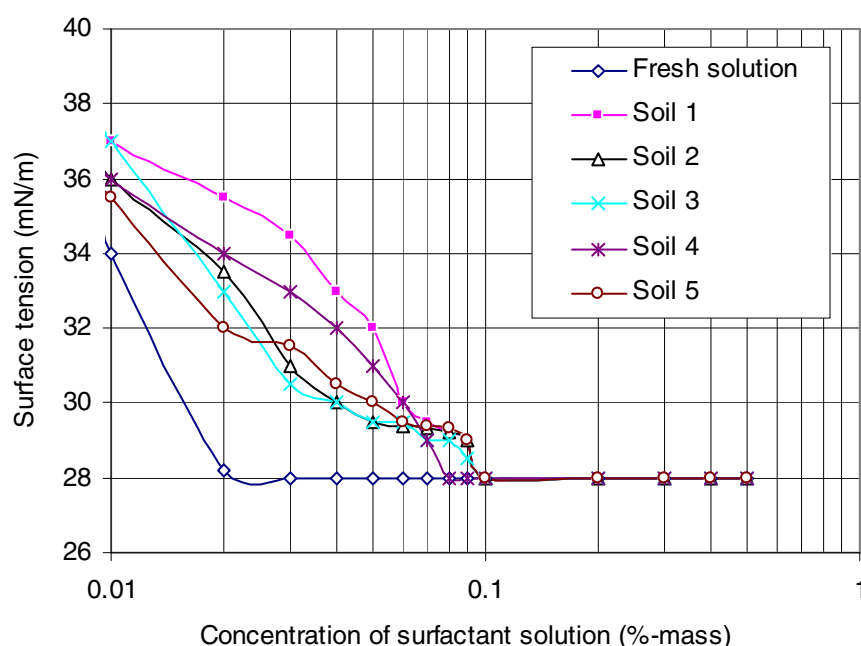


Figure 4.4. Rhamnolipid (prepared in distilled water) sorption in soil

In Figure 4.4, rhamnolipid fresh solution has a CMC of 0.02%-mass and supernatant CMC of 0.008%-mass with Soil – 4 therefore, sorption of 75%. Similarly, lecithin surface tension of 40 mN/m was observed to occur at 0.4%-mass solution and the supernatant has a CMC of 0.9%-mass at the same surface tension thus the loss is about 55.56%. For aescin with CMC of 0.1%-mass showed the greatest loss of 80%. Such loss might reduce its effectiveness in removing oil from contaminated soil. Generally, the effectiveness of surfactant solutions will depend on their surfactant tension reduction ability and CMC at which the sorption to soil was evaluated. The surfactant loss in the different soils was evaluated following the same method and summarized in Table 4.3 to Table 4.4. In the tables  $C_p$  and  $C_s$  are CMC of the fresh and supernatant surfactant solutions.

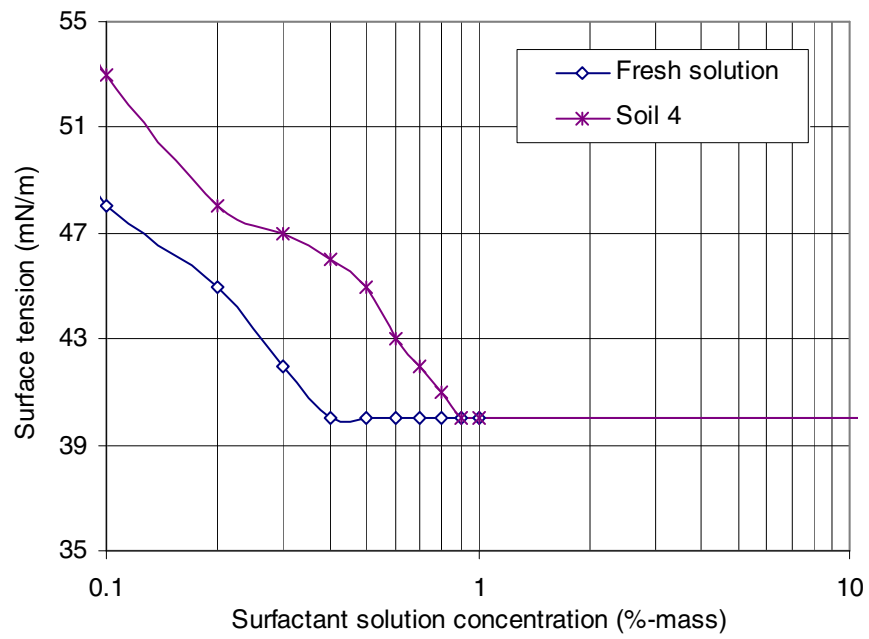


Figure 4.5. Lecithin (prepared in distilled water) sorption in soil

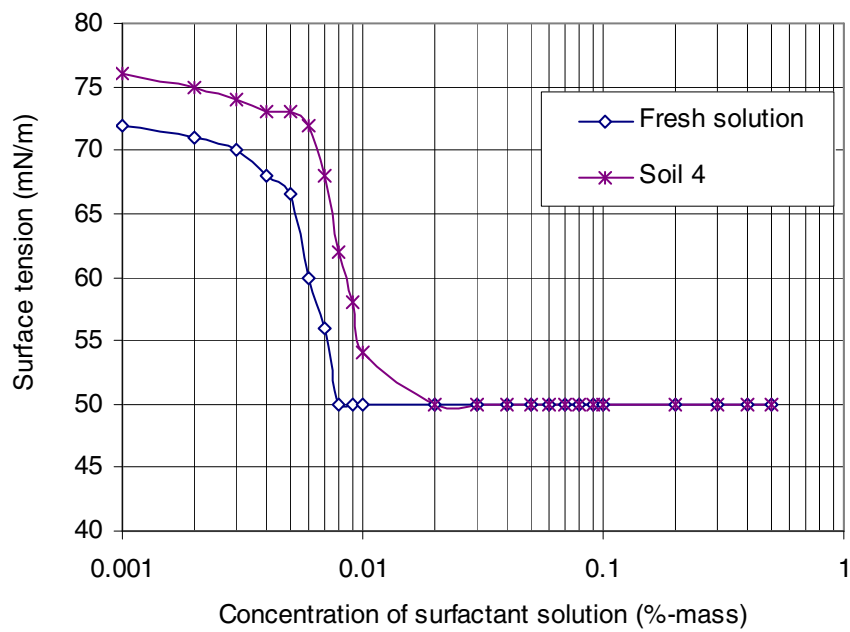


Figure 4.6. Tannin (prepared in distilled water) sorption in soil

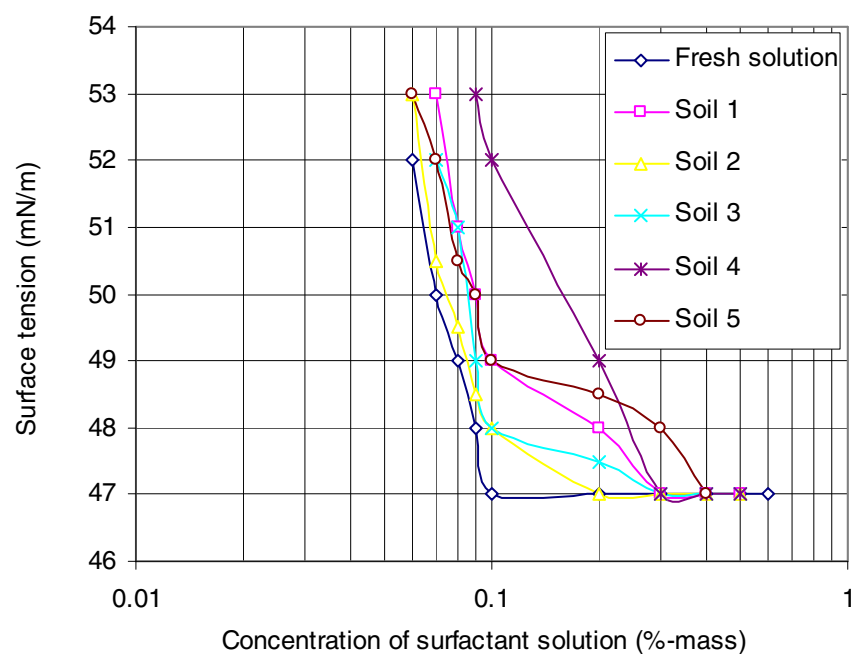


Figure 4.7. Saponin (prepared in distilled water) sorption in soil

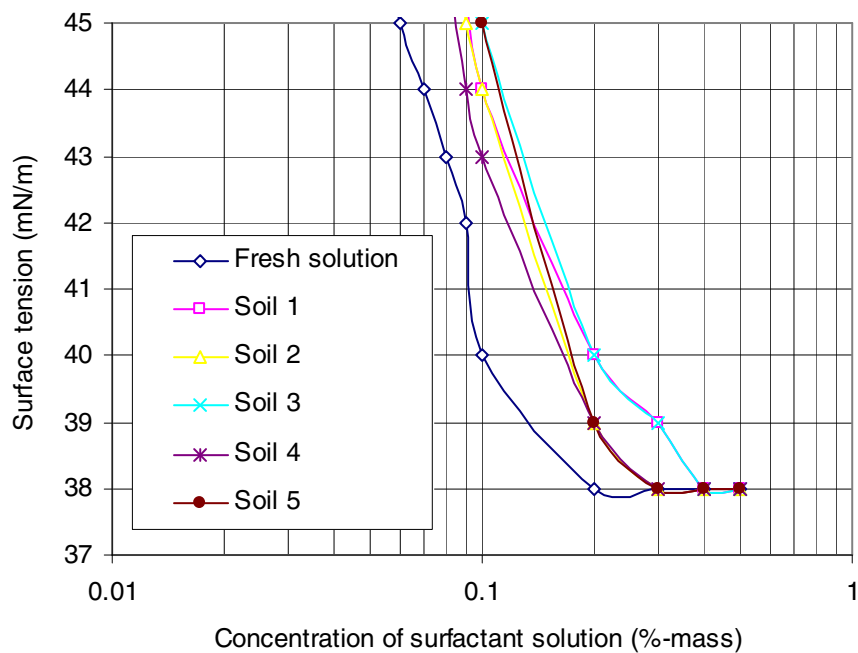


Figure 4.8. SDS (prepared in distilled water) sorption in soil

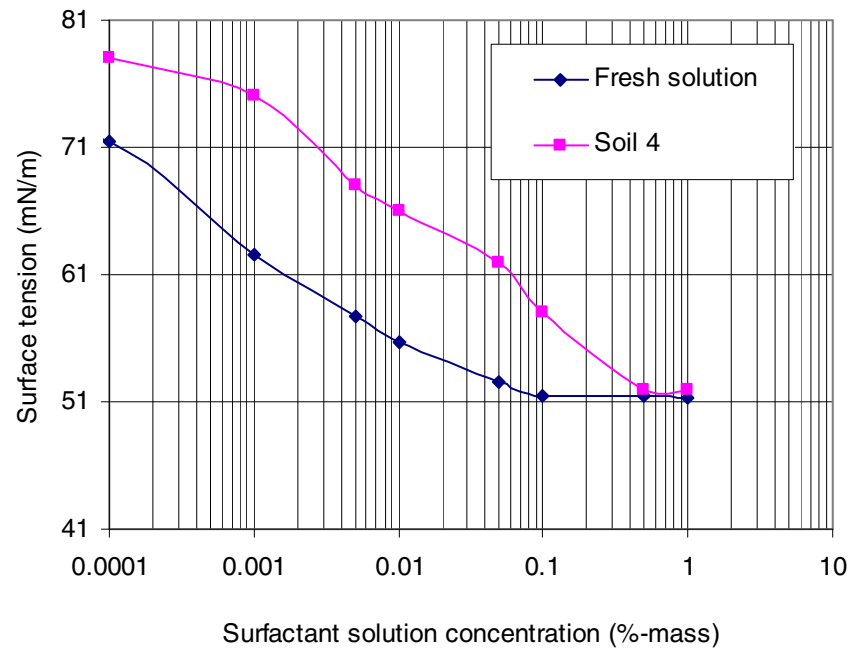


Figure 4.9. Aescin (prepared in distilled water) sorption in soil

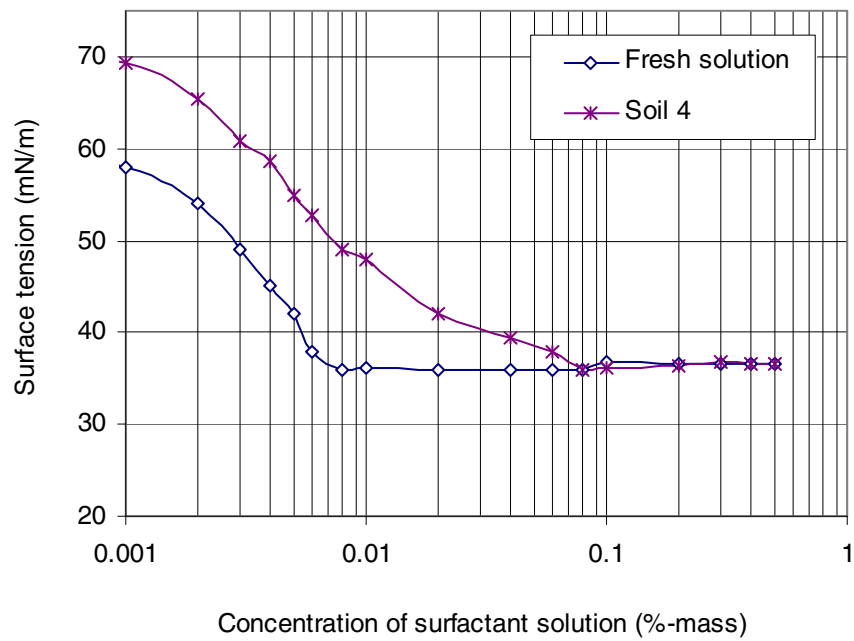


Figure 4.10. Rhamnolipid (prepared in seawater) sorption in soil



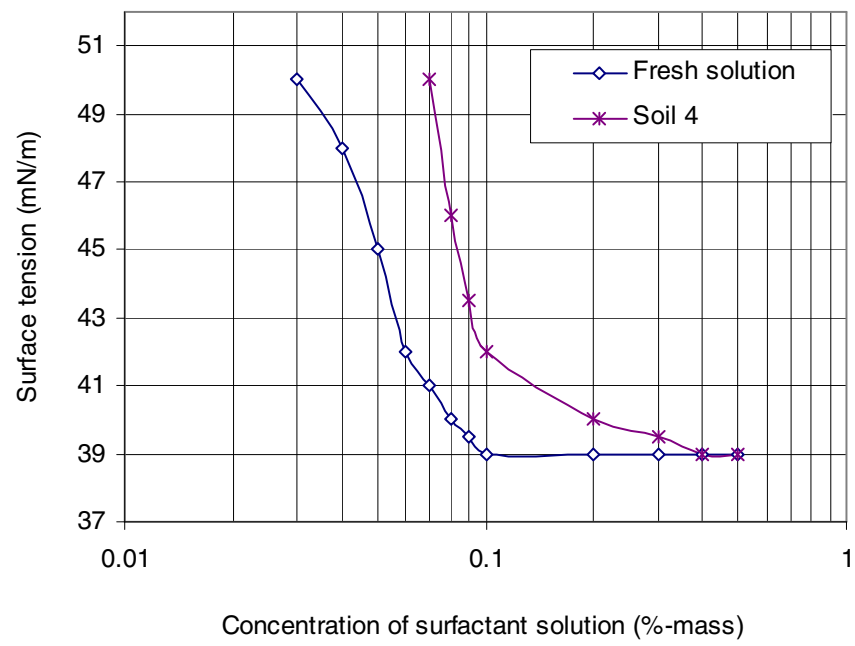


Figure 4.11. SDS (prepared in seawater) sorption in soil

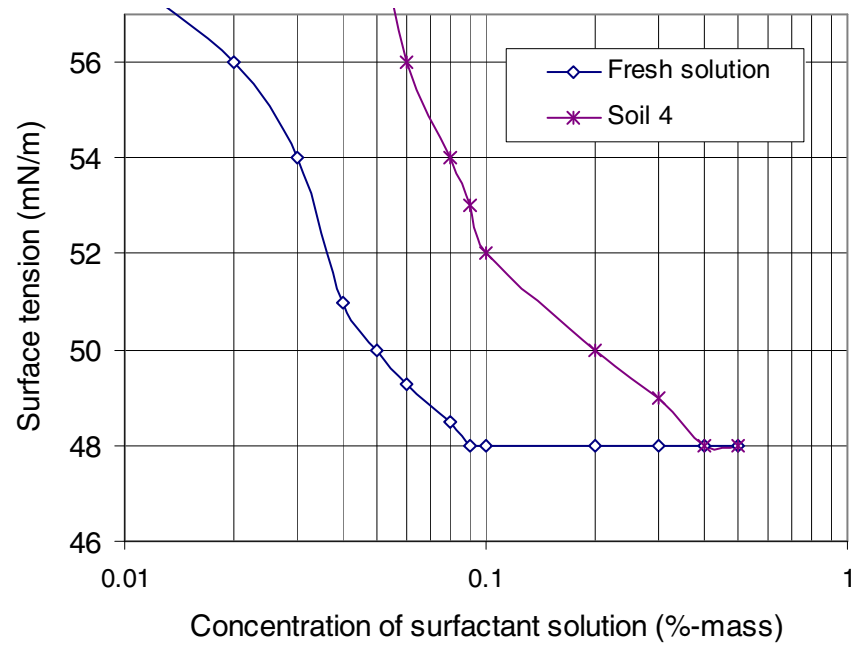


Figure 4.12. Saponin (prepared in seawater) sorption in soil

Table 4.3. Sorption of surfactant prepared with distilled water

		Rhamnolipid	SDS	Aescin	Tannin	Saponin	Lecithin
Soil - 1	CMC <sub>p</sub>	0.02	0.2			0.1	
	CMC <sub>s</sub>	0.09	0.4			0.3	
	Loss (%)	77.78	50.00			66.67	
Soil - 2	CMC <sub>p</sub>	0.02	0.2			0.1	
	CMC <sub>s</sub>	0.1	0.3			0.2	
	Loss (%)	80.00	33.33			50.00	
Soil - 3	CMC <sub>p</sub>	0.02	0.2			0.1	
	CMC <sub>s</sub>	0.1	0.4			0.3	
	Loss (%)	80.00	50.00			66.67	
Soil - 4	CMC <sub>p</sub>	0.02	0.2	0.1	0.08	0.1	0.4
	CMC <sub>s</sub>	0.08	0.3	0.5	0.2	0.3	0.9
	Loss (%)	75.00	33.33	80.00	60.00	66.67	55.56
Soil - 5	CMC <sub>p</sub>	0.02	0.2			0.1	
	CMC <sub>s</sub>	0.1	0.3			0.4	
	Loss (%)	80.00	33.33			75.00	

Table 4.4. Sorption of surfactant prepared with seawater

		Rhamnolipid	SDS	Saponin
Soil - 4	CMC <sub>p</sub>	0.008	0.1	0.08
	CMC <sub>s</sub>	0.08	0.4	0.4
	Loss (%)	90.00	75.00	80.00

In a soil washing system it will be expected that the surfactant that showed less sorption in soil will have greater tendency in removing oil from soil. This is because sorption in soil will lead to the loss of surfactant monomers which may contribute to less formation of micelles. Generally, the CMC of the surfactant solution is a good indicator of surfactant effectiveness in removing oil from a contaminated soil. If surfactant have a low CMC and get in contact with soil, as the concentration of the surfactant solution is

increased beyond the CMC, the surfactant monomers may form more micelles which will replace those ones adsorbed by soil.

#### **4.1.5 Emulsion stability**

A control study was carried out with crude oil and water without surfactants. It was observed that for all the volume ratios tested there was no emulsion formation. The phases separated in less than two seconds after stopping the agitation. This indicated that Ekofisk crude oil could not form emulsions in the absence of surfactants due to its low asphathenes content of 0.03 %-mass (Cormack and Nichols 1977). As the surfactants were added for the subsequent studies, emulsions were formed and volume separations were observed and measured. It was assumed that the emulsions are mesostable; thermodynamically considered to be macroemulsions (Fingas et al. 1999).

##### ***4.1.5.1 Emulsion classifications***

The emulsions formed were observed to be easily diluted in water, while it was not so when diluted in crude oil. This suggests that emulsions were of o/w type. To consolidate this result the electrical conductivities of the emulsions was measured at 15°C. The results showed that the emulsions have different electrical conductivity, which was greater than that of water ( $80 - 200 \times 10^{-6} \text{ S/cm}$ ). As w/o emulsions will not indicate electrical conductivity, it was concluded that the emulsion formed were of o/w type and the surfactants have hydrophilic–lipophilic balance (HLB) in the range of 8–18 (Rosen (1989) and Torres and Zamora (2002)). Aveyard et al. (2003) also noted that HLB could be regarded to be parallel to the wettability of surfactant systems.

The formation of o/w emulsions will favour the application of aqueous surfactant solutions removing oil from soil. This is because the formation of crude oil/water emulsions gives an indication of oil mobilization and solubilization potential of the surfactant solutions. The emulsification effectiveness was taking to be surfactant that shows greater emulsions phase only and/or water phase with less crude oil phase, as concentrations and surfactant solution/crude oil ratio increases. Also, the greater volume of emulsions formed at 0.05%-mass also showed the effective solubilization of crude oil in the surfactants interior micelles.

#### 4.1.5.2 System containing SDS

The results of SDS emulsification of crude oil – water systems are shown in Figure 4.13. For the distilled water, as the volume of crude oil increases, the emulsion phase also increased for surfactant concentration of 0.5 to 5%-mass. At a concentration of 0.05 %-mass, emulsification was not effective and results were similar to those obtained from crude oil-distilled water only test (no surfactant). Therefore, emulsification of SDS in distilled water was observed not to depend only on concentration of solutions but also depend on increase volume of crude oil. The greater emulsification of crude oil as volume fraction of crude oil is increased at concentrations beyond the CMC shows SDS tendency in solubilizing crude oil in the surfactant micelles, which will lead to the enhancement of oil removal from a contaminated soil (Deshpande et al. 1999). In the figures “O” stands for oil phase, “E” is emulsion phase and “W” is for the water phase.

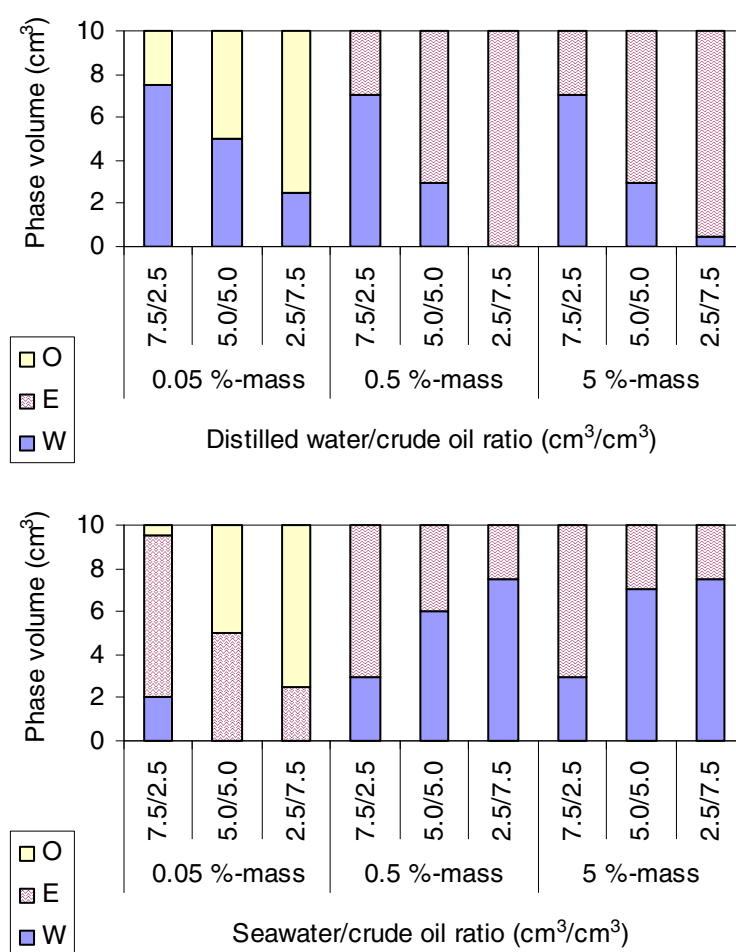


Figure 4.13. Emulsification of crude oil in SDS solution

For the seawater study, similar results were obtained as those of the distilled water. The only difference was at 0.05%-mass with volume ratio of 7.5/2.5, which indicated three phases. The separation of three phases shows the effect of electrolyte on the system. Since the majority of colloidal particles in aqueous dispersions are charged, presence of salt in seawater not only reduce their surface potentials but also lead to coagulation of the particles into flocs which increases the interactions between the surfactants ionic moieties. Even at low electrolyte concentrations, emulsions are stabilized by electrostatic repulsion forces between the droplets covered with the electrical double layers.

#### ***4.1.5.3 System containing rhamnolipid***

The phase separations observed with rhamnolipid in crude oil- distilled water systems were similar to those of SDS as shown in Figure 4.14. However, emulsion phase was observed at 0.05%-mass with volume ratios of 7.5/2.5 and 5.0/5.0. This concentration is within the CMC of rhamnolipid with an interfacial tension of about 4.5 mN/m. Therefore, within the CMC value of rhamnolipid solution, increase in volume ratio of crude oil did not lead to increase in effective emulsification. For the seawater tests, the crude oil and emulsions phases were predominantly observed. This was due to the fact that seawater will reduce the electrical potential of the dispersed oil thereby increasing the interaction between the surfactant ions and counter ions which make rhamnolipid less hydrophilic.

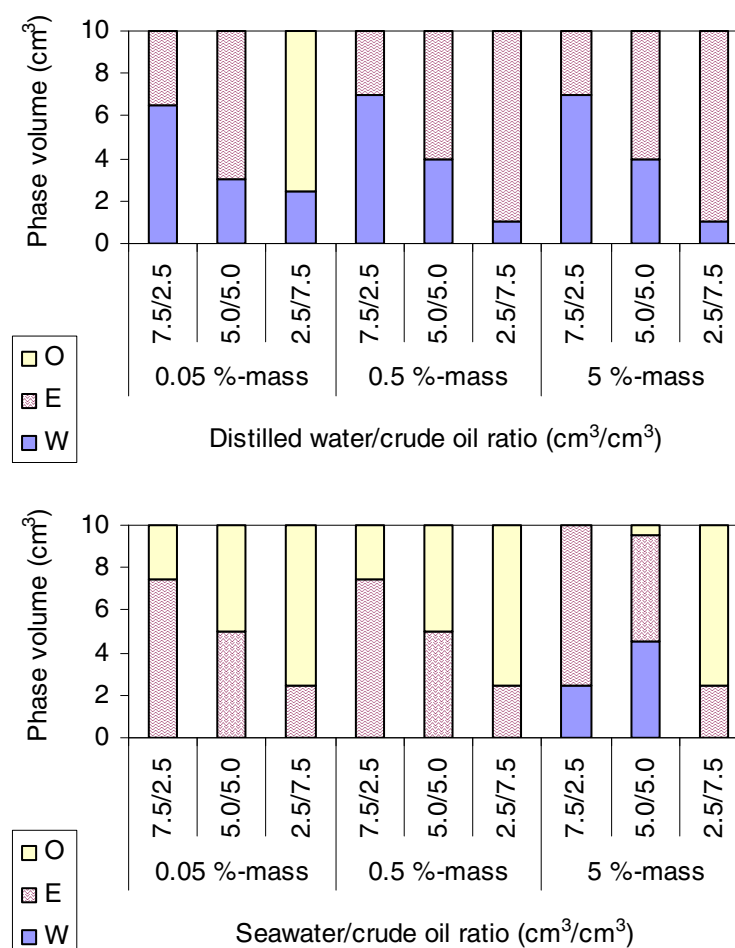


Figure 4.14. Emulsification of crude oil in rhamnolipid solution

#### 4.1.5.4 System containing tannin

Over the range of concentrations and volume ratios tested the following observations were made for crude oil-distilled water system shown in Figure 4.15. The crude oil phases were observed to increase as the crude oil ratio is increased. Water phase reduce as the crude oil volume ratio is increased, and finally, three layers were observed in most of the test. Tannin CMC was at 0.01%-mass solution with an interfacial and surface tension of 4.50 and 50.00 mN/m respectively. The interfacial tension and CMC are similar to those of rhamnolipid, however the three layers formations indicated that they are less stable over the parameters tested. For crude oil –sea water systems, no water phase was observed at crude oil ratios of 7.5. This gives an indication that more surfactant would be needed to emulsify the excess crude oil phase. This study suggests that tannin would not be efficient in separating crude oil from soil due to the excess crude oil phase formed.

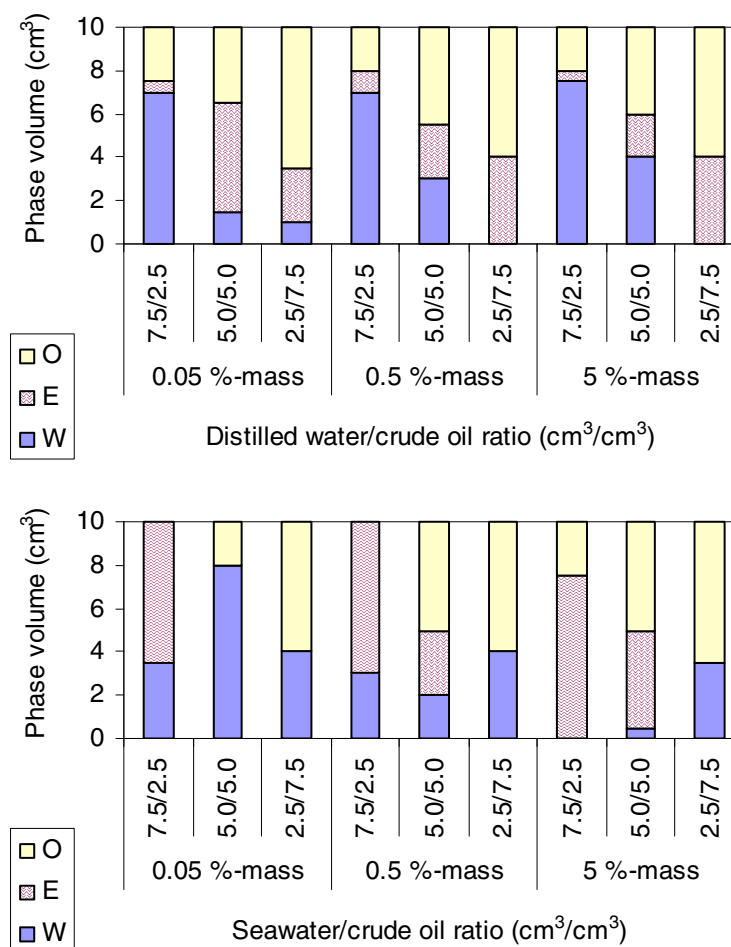


Figure 4.15. Emulsification of crude oil in tannin solution

Generally, the entire phase separation may be attributed to the bulky molecular structure of the tannin. Surfactants with bulky molecular structures have been noted to change the size and shape of micelles (Elvers et al. 1994). As the concentrations tested in this study are greater than tannin CMC values, more change in micelle shape and size would be expected. This phenomenon of change in surfactant micelle shape and size will lead to the instability of tannin solution thereby providing the fast separation of three different layers.

#### 4.1.5.5 System containing saponin

Saponin emulsification in distilled water-crude oil systems showed that as crude oil volume ratio increases emulsification reduces (Figure 4.16). The greater emulsifications observed at volume/mass ratios of 7.5/2.5 and 5.0/5.0 showed the possibility of saponin

solubilize crude oil at concentrations lower and greater than saponin CMC values of 0.1%-mass. However, the amount of crude oil used should be moderate to avoid the formation of excess crude oil phase. In the case of crude oil-seawater study, emulsification was observed to mainly depend on the surfactant solution concentration and volume fraction of surfactant. The overall three phases noted was also due to the nature of the saponin with bulky chemical structure, which might contribute to the change in the shape and size of micelles.

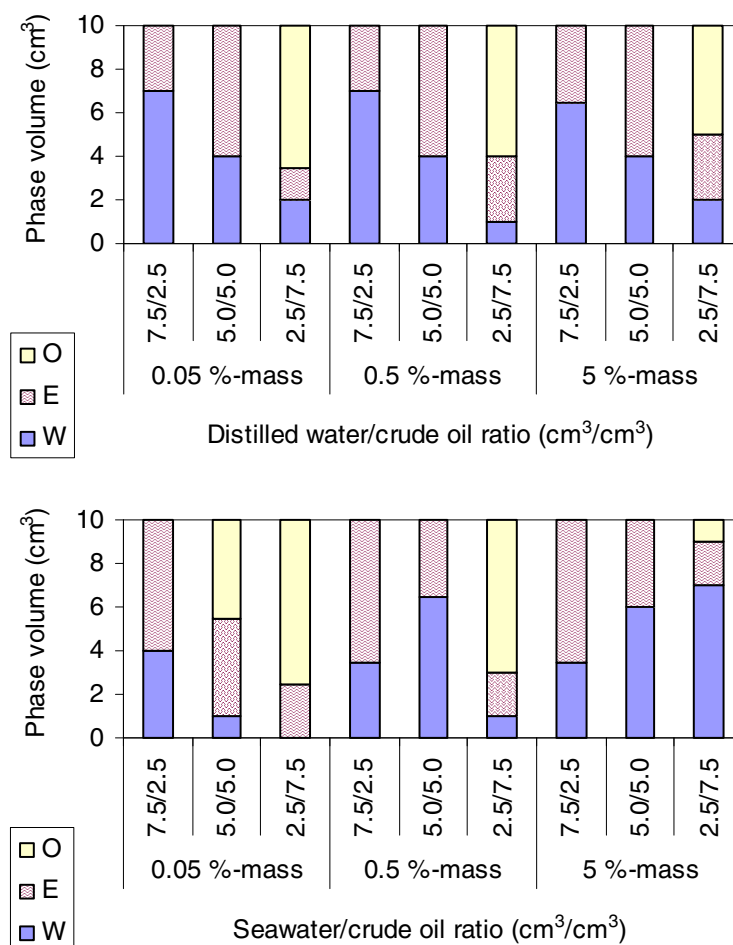


Figure 4.16. Emulsification of crude oil in saponin solution

#### 4.1.5.6 System containing aescin

Results of these studies indicated that crude oil – distilled water and crude oil –seawater systems show similar emulsion formation (Figure 4.17). The excess crude oil phases remaining at volume/mass ratio of 2.5/7.5 indicated that the aescin might not be effective on crude oil removal from soil. The results of this study agrees with the work



in Pekdemir et al. (1999) that the emulsification efficiency of oil and aescin prepared in either distilled or seawater solutions increases as the volume of aescin solution is increased.

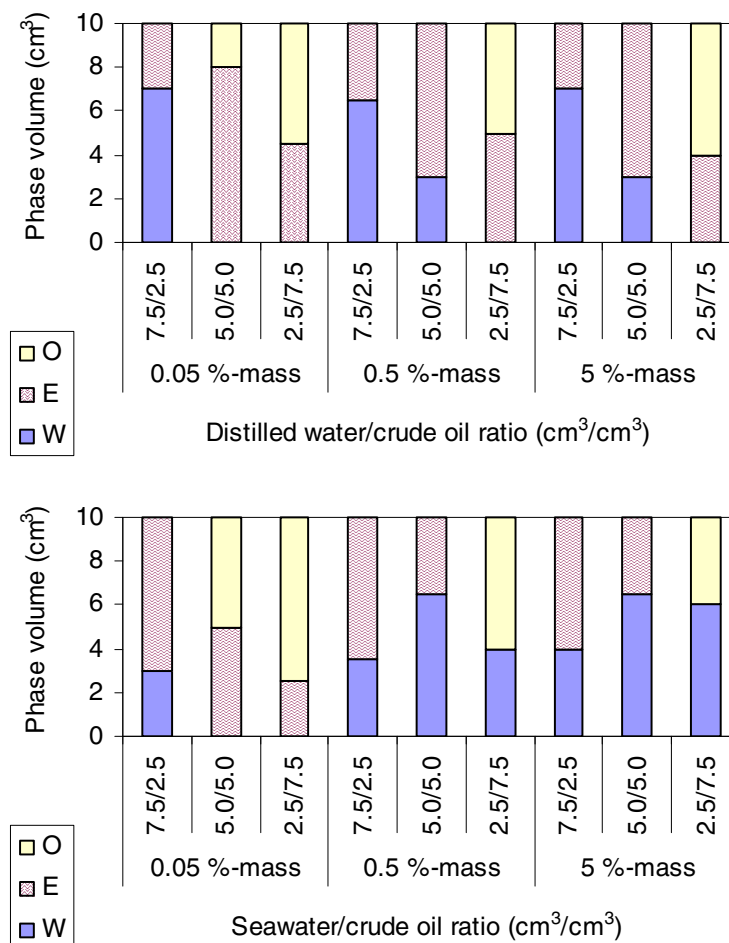


Figure 4.17. Emulsification of crude oil in aescin solution

#### 4.1.5.7 System containing lecithin

Lecithin emulsions formed three layers in most cases. The excess crude oil and emulsions phases were noticed with 5 %-mass solutions at volume ratios of 5/5 and 2.5/7.5 (Figure 4.18). The emulsification effectiveness of lecithin was observed to be reducing in crude oil seawater systems. With 0.05%-mass solutions the emulsions separated to seawater and crude oil phases. Lecithin has a bulky molecular structure; its solutions were also noted to be more viscous than the other surfactants tested. In soil washing lecithin interfacial contact with crude oil might not be as good as the other surfactants. Therefore, the formation of excess crude oil phase observed in the studies

will not favour the removal of oil from soil.

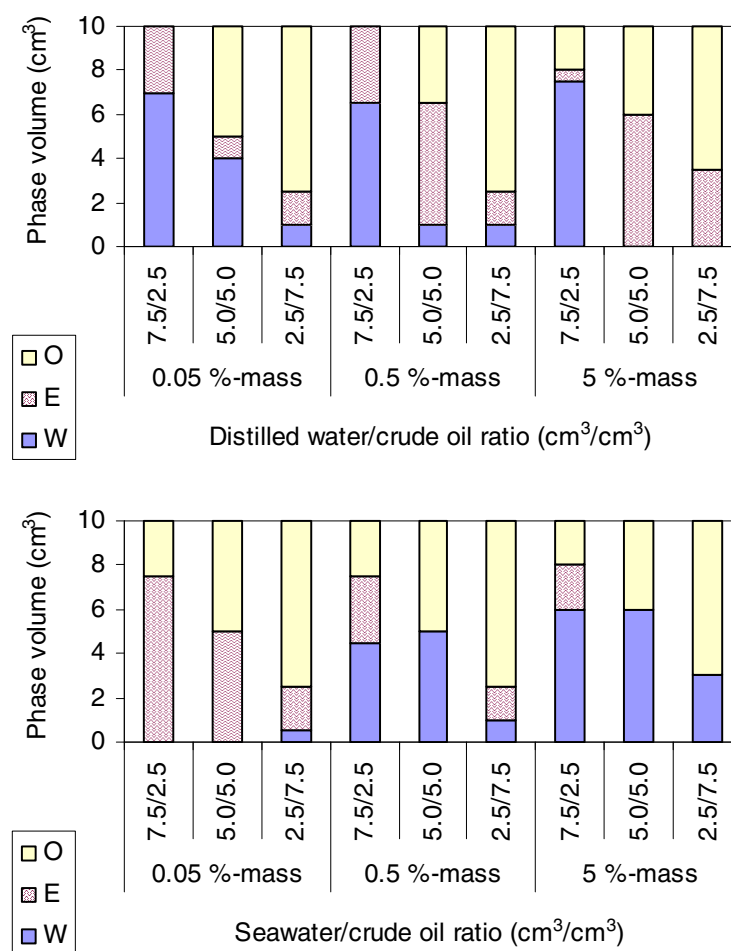


Figure 4.18. Emulsification of crude oil in lecithin solution

Generally, emulsions aid in the remediation process by increasing the surface area between the surfactant and oil. This allows the surfactant to react easier in absorbing the non-polar oil into the micelles interior, thus increasing the mixture solubility. If the emulsion is carried easily by the surfactant, it will aid in the removal of the micelle contaminant combination from the soil and surfactant. However, emulsion will hinder the progression of oil removal from soil if the thickness of the emulsion layer becomes too thick. This will act as a barrier that isolates the oil from the surfactant solutions. It also can clog the pore spaces of soils thus preventing the rapid extraction of the oil/micelle mixture.

#### 4.1.6 Solubilization

The results of the solubilization of crude oil with surfactant solutions are presented in Figure 4.19 and Figure 4.20 for distilled and seawater respectively. It is seen that SDS in seawater have the maximum solubility of about 180 mg/liter between the concentration of 0.1 and 0.5%-mass. It can be argued that only a maximum of about 0.11% of the crude oil could be solubilized in aqueous surfactant solutions of the tested concentrations. Such low solubilisation could be expected for two reasons: (1) the surfactant concentrations tested was not much greater than the CMC values, (2) crude oil is highly hydrophobic and complex in nature, it comprises more than 50 to 80% aliphatic hydrocarbons which are generally known to have low solubility in water (NAS 1985).

The solubilization effectiveness of crude oil into the micelles of surfactant solutions was assumed to occur above the surfactant solution CMC. As indicated in Figure 4.19 and Figure 4.20, most of the surfactants did not show micelle solubilization because their solubilisation plot reduces or remain constant after reaching the CMC values. Therefore, solubilisation ratio, which is the slop of the plot beyond the CMC and represents the amount of crude oil solubilize per surfactant micelle concentrations was determined and presented in Table 4.5.

Table 4.5. Solubilization ratio of surfactant solution (ppm)

Surfactants	Distilled water	Seawater
Aescin	$57.88 \times 10^{-4}$	$15.34 \times 10^{-4}$
Lecithin	$7.92 \times 10^{-4}$	$8.67 \times 10^{-4}$
Rhamnolipid	$57.88 \times 10^{-4}$	$18.43 \times 10^{-4}$
Saponin	$36.66 \times 10^{-4}$	$15.12 \times 10^{-4}$
SDS	$1.19 \times 10^{-4}$	$8.53 \times 10^{-4}$
Tannin	$34.73 \times 10^{-4}$	$13.07 \times 10^{-4}$

The solubilisation ratio of rhamnolipid in Table 4.5 implied that  $57.88 \times 10^{-4}$  ppm of crude oil would solubilize in 1 ppm of rhamnolipid solution. This solubilization ratio could be used to assess the effectiveness of surfactants in removing crude oil from

contaminated media. Surfactants that have more solubilisation ratio give an indication on its ability to recover oil from soil or water body.

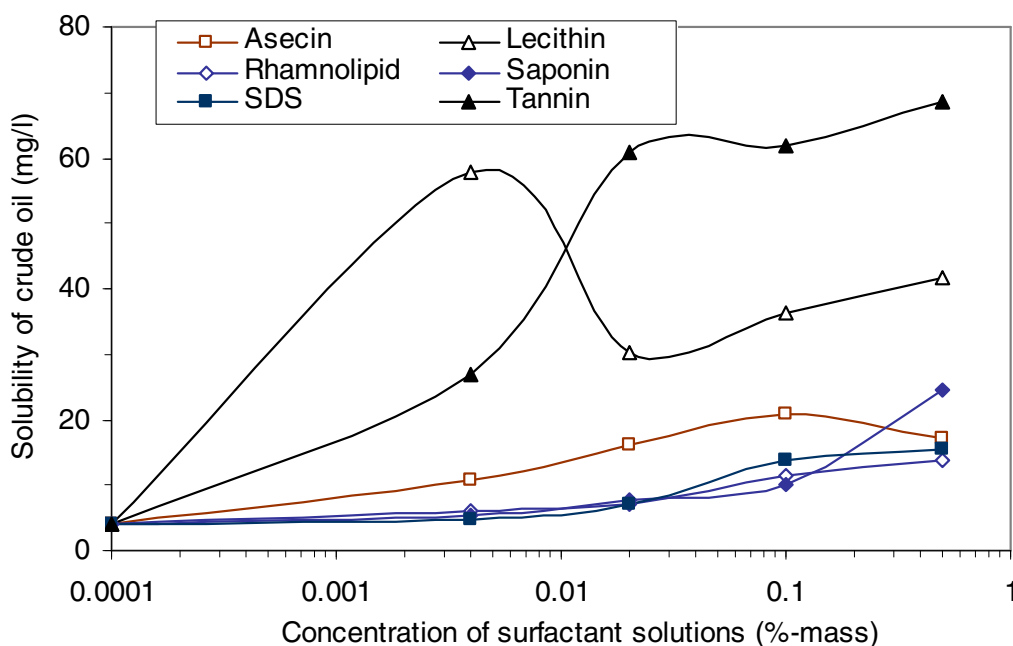


Figure 4.19. Solubility of crude oil in aqueous surfactant solutions prepared in distilled water at 20-22<sup>0</sup>C with error of  $\pm 8\%$ .

The base case study (water only) conducted showed that crude oil solubilization in distilled water and seawater was 1.54 and 18.36 mg/liter respectively. Generally, rhamnolipid and SDS also showed greater solubilisation of crude oil in the seawater than that in distilled water (Figure 4.19 and Figure 4.20). The salts in seawater decrease the repulsion between similar charged ions in the surfactant head group. Therefore, as rhamnolipid and SDS are ionic surfactant; in seawater its aggregation would increase due to the compression of the electrical double layer that surrounds their ionic heads thus, enhancing greater solubilisation.

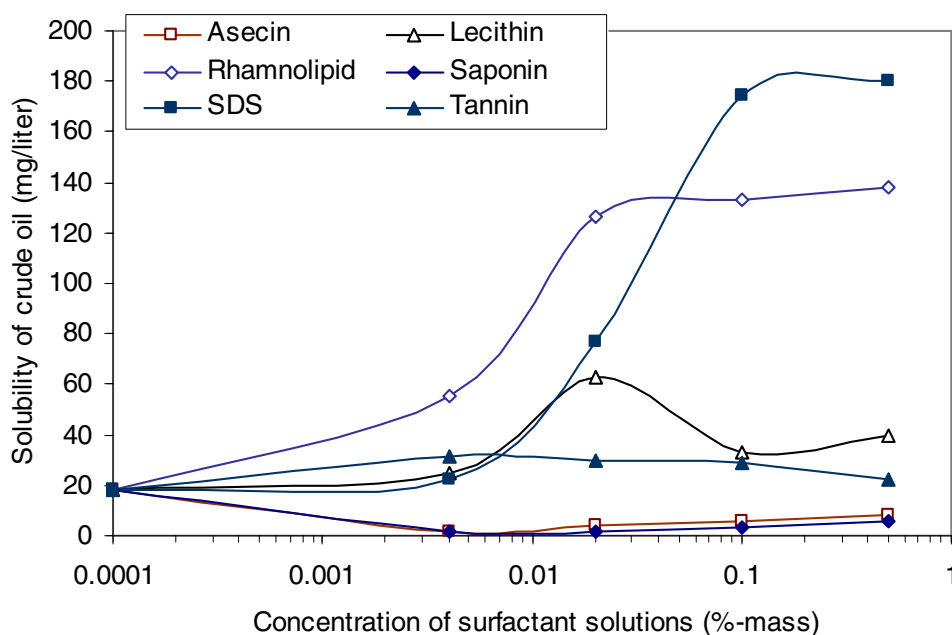


Figure 4.20. Solubility of crude oil in aqueous surfactant solutions prepared in seawater at 20-22<sup>0</sup>C with error of  $\pm 8\%$ .

For Tannin, with CMC of 0.01%-mass, it is noted from Figure 4.19 that as concentration increase up to 0.02 %-mass there is a significant increase in solubilization of 61 mg/liter (0.037%) and 31 mg/liter (0.019%) in distilled water and seawater, thereafter change in solubilisation was not significant. This phenomenon may be attributed to changes in tannin micelles, due to concentration variation, which might lead to the change in the size or shape of micelles. Solubilization causes an increase in micelles aggregation number. As more crude oil solubilize in the micelles, the aggregation number continues to increase until a solubilisation limit which is the point at which the solubilization remains constant indicating that surfactant have reached its solubilization limit.

Aescin prepared with distilled water showed a considerable solubilization at the neighbourhood of its CMC. This suggests micelles solubilisation. The saponin and aescin plots in Figure 4.20 showed the effects of salts towards the solubilization effectiveness of the surfactants. Solubilization in seawater only was greater than those of the two surfactants, which yielded less than 10 mg/liter over the range of concentration tested. Lecithin solubilization reaches a maximum value of 59 and 61 mg/liter at 0.004 and 0.02%-mass for distilled water and seawater respectively and then remains constant. This trend may also be attributed to change in micelles shape and size

as the concentration is increased. According to Sikdar and Irvine (1998), the size and shape of surfactant micelles can have significant effect on their phase behaviour as well as their capacity to solubilize organic compounds. As this thesis does not investigate on surfactants micelles structures and sizes, work relating to this aspect has been reported in literature by Elvers et al. (1994).

#### **4.1.7 Surfactant precipitation in seawater**

The result of this experiment shows that seawater did not reduce the concentrations of saponin and SDS in solution. However, SDS solubility in seawater was not as fast as when prepared in distilled water. SDS solutions coalesce and appear turbid, after about two hours the solution becomes clear. This study indicated that salt does not affect saponin but will considerably delay the solubility of SDS. For rhamnolipid, there was settling of materials at the bottom of the volumetric cylinder. When tested with the spectrophotometer at different time intervals, it was noticed that the concentration of rhamnolipid starts reducing after the 18 hour.

The precipitation of rhamnolipid may lead to the loss of micelle concentrations. Such loss may adversely affect soil washing in columns. This is possible if the time of soil washing is longer than (18 hours). Above this time, rhamnolipid will settle down and the concentration of solution passing through soil column will be reducing. The knowledge of precipitation of rhamnolipid is relevant in selecting contact time and flow rate required of surfactants in washing a contacted soils in columns.

#### **4.1.8 Conclusions**

##### *Surface and interfacial tension*

- The result of the surface tension measurement for distilled water prepared solutions indicated that the CMC of rhamnolipid, aescin saponin, lecithin, tannin and SDS occur at solution concentrations of 0.02, 0.1, 0.1, 0.4, 0.008 and 0.2%-mass respectively
- The solutions prepared with seawater have CMC at 0.008, 0.20, 0.08, 0.40, 0.01 and 0.10%-mass for rhamnolipid, aescin saponin, lecithin, tannin and SDS respectively
- The interfacial tension between crude oil and distilled water was measured as 25

mN/m

- The reduction of interfacial tension indicates the ability of surfactants to remove oil from soil
- This reduction will increase the contact angle and the reduction of the capillary force holding crude oil and soil together which result to the mobilization of oil
- Rhamnolipid and tannin would show more potential in oil removal from soil than the other surfactant solutions, this is because they have low CMC value that was able to reduce water interfacial tension to 4.5 mN/m. However, lecithin shows less potential in comparison with the other biosurfactants

### *Foaming*

- This study was carried out in duplicate and the results were reproducible at 8%.
- Saponin has greater initial foaming ability than rest surfactant
- Saponin foams was not as stable as that of SDS and after 5 minutes saponin foams were less than those of SDS
- SDS foaming was more stable over the tested range of concentrations, followed by aescin and then saponin

### *Sorption to soil*

- In a soil washing system it will be expected that the surfactant that showed less sorption in soil will have greater tendency in removing oil from soil
- This is because sorption in soil will lead to the loss of surfactant monomers which may contribute to less formation of micelles
- The CMC of the surfactant solution is a good indicator for surfactant effectiveness in removing oil from a contaminated soil
- If surfactant have a low CMC and get in contact with soil, as the concentration of the surfactant solution is increased beyond the CMC, the surfactant monomers may form more micelles which will replaced those ones adsorbed by soil

### *Emulsification*

- Ekofisk crude oil could not form emulsions in the absence of surfactants due to its

low asphathenes content of 0.03%-mass

- As the surfactants were added mesostable emulsions were formed
- The emulsions formed were easily diluted in water, while it was not so with crude oil thus emulsions were oil-in-water type
- The surfactants have hydrophilic–lipophilic balance (HLB) in the range of 8–18
- The formation of o/w emulsions will favour the application of aqueous surfactant solutions removing oil from soil
- The emulsification effectiveness was due to the surfactant that shows greater emulsions phase only and/or water phase with less crude oil phase, as concentrations and surfactant solution/crude oil ratio increases
- The entire phase separation may be attributed to the bulky molecular structure of the tannin, saponin, lecithin and aescin
- Lecithin has a bulky molecular structure; its solutions were also noted to be more viscous than the other surfactants tested.
- In soil washing lecithin interfacial contact with crude oil might not be as good as the other surfactants. Therefore, the formation of excess crude oil phase observed in the studies will not favour the removal of oil from soil.
- Emulsions will aid in the remediation process by increasing the surface area between the surfactant and oil. This allows the surfactant to react easier in absorbing the non-polar oil into the micelles interior, thus increasing the mixtures solubility. If the emulsion is carried easily by the surfactant, it will aid in the removal of the micelle contaminant combination from the soil and surfactant.
- Emulsion will hinder the progression of oil removal from soil if the thickness of the emulsion layer becomes too thick. This will act as a barrier that isolates the oil from the surfactant solutions. It also can clog the pore spaces of soils thus preventing the rapid extraction of the oil/micelle mixture

### *Solubilization*

- SDS has the maximum solubility of about 180 mg/liter in seawater
- Maximum of about 0.11% of the crude oil could be solubilized in aqueous surfactant solutions of the tested concentrations
- The solubilization effectiveness of crude oil into the micelles of surfactant solutions was assumed to occur above the surfactant solution CMC



- The crude oil solubilization in distilled water and seawater was 1.54 and 18.36 mg/liter respectively
- Rhamnolipid and SDS also showed greater solubilisation of crude oil in the seawater than that in distilled water
- The salts in seawater decrease the repulsion between similar charged ions in the surfactant head group
- This experiment was repeated in duplicate with a repeatability range of  $\pm 8\%$ .

### *Precipitation*

- The result of this experiment shows that seawater did not reduce the concentrations of saponin and SDS
- SDS solubility in seawater was not as fast as when prepared in distilled water
- SDS solutions coalesce and appear turbid, after about two hours the solution becomes clear
- Salt does not affect saponin but will considerably delay the solubility of SDS
- For rhamnolipid, there was settling of materials at the bottom of the volumetric cylinder, the precipitation of rhamnolipid may lead to the loss of micelle concentrations
- The knowledge of precipitation of rhamnolipid gives an idea in selecting contact time and flow rate required of surfactants in washing a contacted soils in columns

## **4.2 Test tube washing**

Test tube washing was used to establish the basis of soil washing. The screening of biosurfactants was first examined with the non-weathered samples of Soil – 4 (Section 4.2.1). Based on the findings, the washing of different weathered soil samples was undertaken in Section 4.2.2.

### **4.2.1 Screening of surfactant solutions**

This section presents results on the ability of the biosurfactants to remove crude oil from Soil – 4. The reason for using non-weathered contaminated soil (Soil – 4) was due to the inadequate availability of literature on crude oil removal from soil using biosurfactants. Thus, working with Soil – 4 which consist of most of the different soil particles sizes, give a general idea of the biosurfactant's efficiency at low concentrations compared to higher solution concentrations studied by Deshpande et al. (1999) and Harvey et al. (1990).

The results of crude oil removal are presented in Figure 4.21 to Figure 4.25. The presentation of Figure 4.21 to Figure 4.25 was based on the most influential parameter on crude oil removal from soil with surfactant solutions. This was determined by finding the difference between the lowest and highest amount of crude oil removed from soil for each surfactant solutions.

#### ***4.2.1.1 Effect of washing temperature***

The results of the effect of washing temperature on crude oil removal are shown in Figure 4.21. It can be seen that there was variation in crude oil removal with temperature for all the surfactant solutions, except lecithin. This characteristic exhibited by lecithin may be due to its gel like appearance with a low reduction in surface and interfacial tension. As interfacial tension of oil/surfactant system does not have correlation with temperature (Jokuty et al. 2000), the crude oil removal as temperature increases is thought to be result of the reduction in the viscosity of crude oil. Thus, an increase in temperature positively influenced crude oil removal from the contaminated soil. The rhamnolipid and SDS had a constant crude oil removal above 20<sup>0</sup>C; the same

applied to saponin between 35 and 50°C. Aescin and tannin showed a linear relationship of crude oil removal with temperature increase, as seen between 35 and 50°C, indicating that more crude oil may be removed if the washing temperature is increased beyond 50°C. However, washing at greater temperatures may not be cost effective and environmentally friendly, since the volatile components of crude oil may evaporate thereby causing more environmental damages.

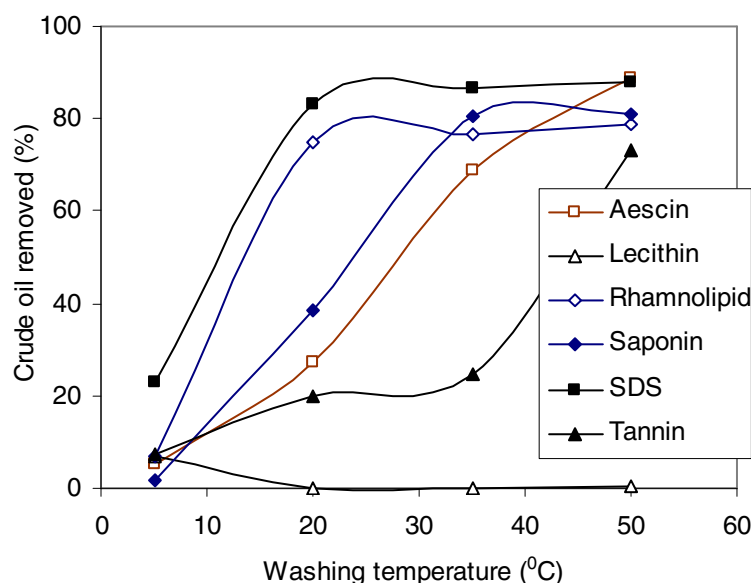


Figure 4.21. Crude oil removal as function of temperature. Washed with 20 cm<sup>3</sup> 0.1%-mass solution, shaken at 200 strokes/minute for 20 minutes.

#### 4.2.1.2 Effect of concentration of surfactant solutions

The solubilization study conducted in Section 3.2.4.6 and was used to demonstrate the amount of crude oil that could be solubilized by the surfactant solutions. To fully understand if solubilisation of crude oil by surfactant solutions is responsible for oil removal from the contaminated soil, some soil washing test were carried out by the aqueous surfactant solutions at varying concentrations including zero concentration (distilled water). The crude oil removed from the soil by water only was about 39% (Figure 4.22). As the surfactant solution concentration was increased to 0.004%-mass, all the surfactant solutions showed an enhancement in crude oil removal. This trend was expected, since the force of attraction between soil and crude oil would be reduced due to the increase in contact angle and change in wettability of the system because of the presence of surfactant.

With the crude oil content of 91.15 mg per gram of Soil – 4 (Section 3.1.3), more than 90 % of the crude oil was removed with 0.5 %-mass solutions of SDS. This crude oil removal was greater than the maximum solubility of 0.11% obtained with 0.5%-mass solution of SDS (Section 4.1.6). Therefore, it was conclude that solubilisation mechanisms discussed in the work of Deshpande et al. (1999), Cheah et al. (1998) and Mulligan et al. (2001c) was not responsible for the crude oil removal from the contaminated soil. The removal of crude oil may be attributed to reduction of surface and interfacial tensions of surfactant solutions. This contributes to the increase in the mobility of crude oil and consequently enhances their separation from soil.

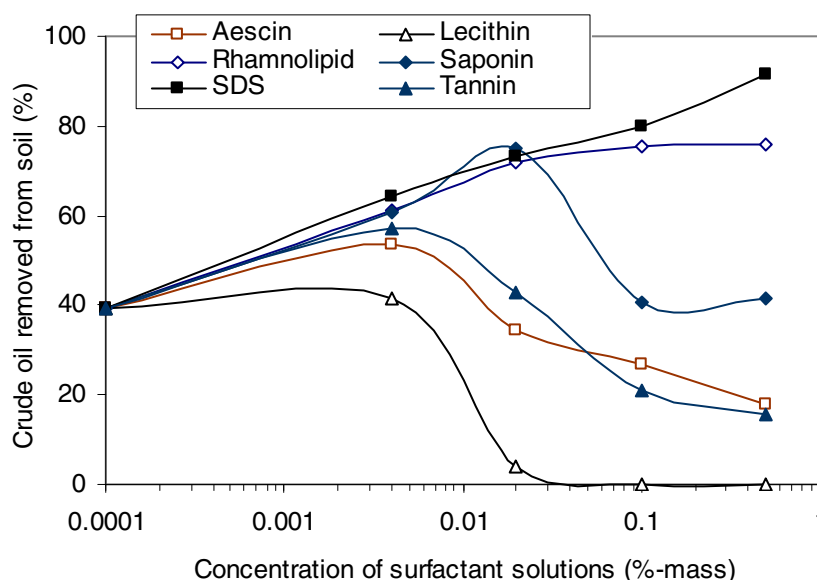


Figure 4.22. Crude oil removal as function of concentration of surfactant solutions. Washed at 20°C with 20 cm<sup>3</sup> solution, shaken at 200 strokes/minute for 20 minutes.

At concentration of 0.02 %-mass and beyond, aescin, lecithin, saponin and tannin, removal of crude oil was reduced. Although these biosurfactants are able to reduce water-crude oil interfacial tension as well as showing certain solubilization as concentration increases (Figure 4.22), their maximum crude oil removal was achieved with either 0.004 or 0.02 %-mass. This result agrees with the work of Abdul et al. (1990) that surfactant solution may not enhance the removal of oil from soil at concentrations greater than their CMC value. Therefore, maximum crude oil removal was obtained at concentrations below the CMC, suggesting that crude oil removal may be due to mobilization, which occur because of the reduction of interfacial tension.

The low removal of crude oil by aescin, lecithin, saponin and tannin at greater concentration, may also be attributed to the change in micelle shape and sizes as noted by Elvers et al. (1994). This author suggests that surfactants with bulky molecular structure often lead to change in micelle shape and size thus, causes micelle instability and reduction of detergency. Since certain biosurfactant does not show greater crude oil removal as concentration increases, the soil washing study suggests that surfactant removal of oil from soil may depend on the surfactant properties and the combined behaviour of surfactant/crude oil/soil systems.

#### 4.2.1.3 Effect of shaking speed

The results of the effect of shaking speed shown in Figure 4.23 indicate that as the shaking speed is increased from 80 to 200 strokes/minute, crude oil removal was enhanced using aescin, rhamnolipid, saponin and SDS. This removal is due to the displacement of oil in the soil surface by the surfactant solutions. This was achieved due to the effect of shaking which generates attrition and abrasion forces in the test tube. As shaking speed is increased, more surface area of the contaminated soil is exposed to the surfactant solution for effective displacement. For tannin, there was no significant enhancement in crude oil removal between the first and the fourth parameter levels tested.

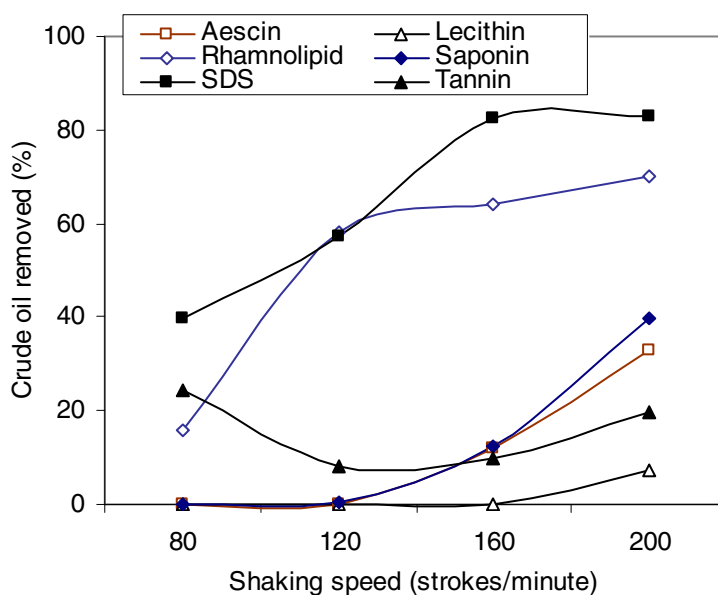


Figure 4.23. Crude oil removal as function of shaking speed. Washed at 20°C with 20 cm<sup>3</sup> 0.1%-mass solution for 20 minutes.

#### 4.2.1.4 Effect of volume of surfactant solution

As indicated in Figure 4.24, change in volume of surfactant solutions shows a corresponding increase in crude oil removal with tannin, rhamnolipid and SDS. The variation of volume of surfactant solutions was used to facilitate the interfacial contact of the crude oil and surfactant. Thus enhancing the penetration of surfactant into the interface between the crude oil and soil. Crude oil removed by aescin and saponin showed a peak at 10 cm<sup>3</sup>, then reduces as volume increased from 15 to 20 cm<sup>3</sup>. It was concluded that 10 cm<sup>3</sup> of the solutions are sufficient to create maximum interaction with the contaminated soil. Lecithin showed a zero percent constant crude oil removal through out the range of volume tested, indicating that any increase in the volume did not enhance the removal of crude oil.

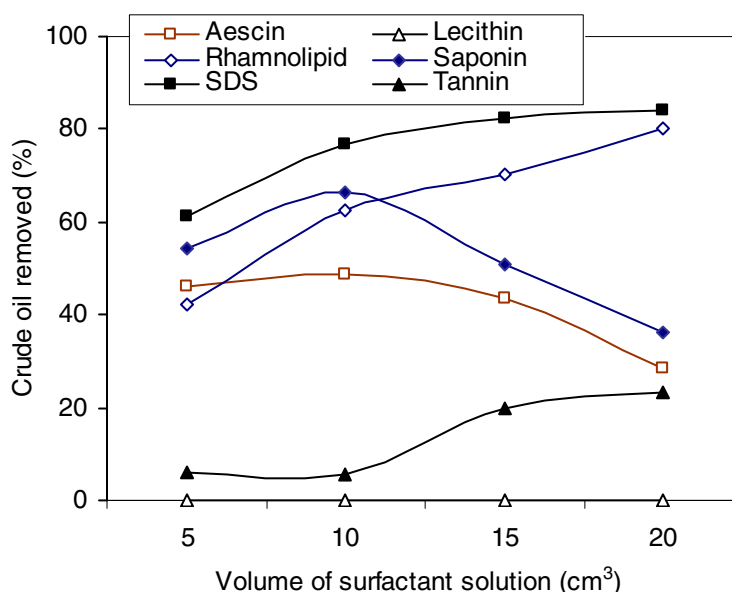


Figure 4.24. Crude oil removal as function of volume of washing solutions. Washed at 20°C with 0.1%-mass solution, shaken at 200 strokes/minute for 20 minutes.

#### 4.2.1.5 Effect of washing time

Increasing washing time showed an increase in crude oil removal for certain surfactant solutions (Figure 4.25). Rhamnolipid and SDS showed a significant crude oil removal between 5 and 10 minutes and thereafter was constant. Maximum crude oil removal with saponin was at 20 minutes (48%). This removal was less than that of rhamnolipid at 5 minutes. Rhamnolipid crude removal was twice that of saponin over the range of

washing time. Crude oil removal between the first and the fourth levels of tannin and lecithin were within the experimental error range. Critical examination of Figure 4.25 showed that the range of crude oil removal between the first and fourth parameter levels by all the surfactant solutions indicated the least influence on crude oil removal. Such trend in oil removal have been noted by Harvey et al. (1990) in washing the Exxon Valdez crude oil spill from Alakan gravelsa at different temperature of 30 and 50°C. The authors pointed out that increase in contact time (from 1 to 2 minutes) between the surfactant solution and the contaminated soil has little effect on crude oil removal. Also, maximum oil removal was achieved in one minute at both temperatures which suggest that surfactant act quickly to separate the oil from soil surface into the bulk water phase. Therefore, it was considered that another test need to be conducted to observe the effect of washing time on crude oil removal at a time of one-minute.

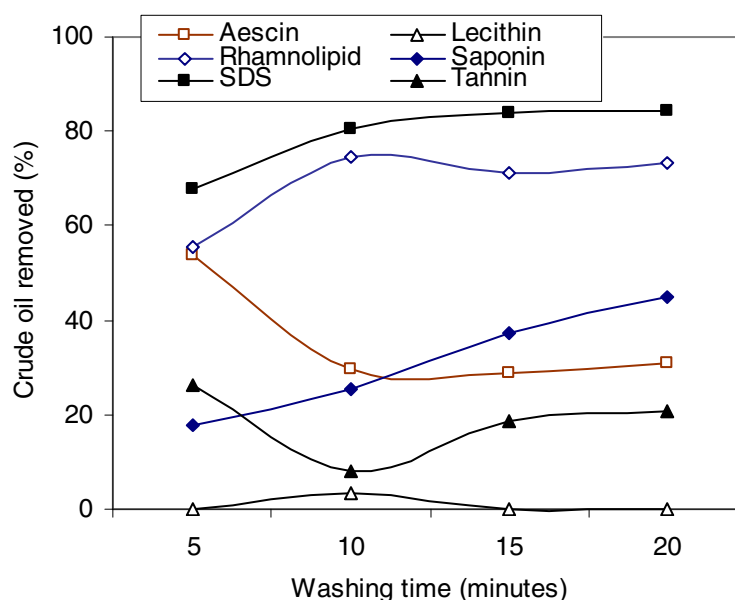


Figure 4.25. Crude oil removal as function of washing time. Washed with 20 cm<sup>3</sup> 0.1%-mass solution at 20°C shaken at 200 stroke/minute.

#### 4.2.1.6 One-minute washing

In the follow up to Section 4.2.1.5, sixty-second washing was conducted at different temperatures. Since the effect of washing time was observed to be the least influential parameter on oil removal, the temperature variation was chosen for the sixty second washing because it shows an effective oil removal in Figure 4.21. Rhamnolipid and SDS were only examined because their crude oil removal during the effect of

temperature showed almost a constant value after 20°C (Figure 4.21) and at 10 minutes (Figure 4.25).

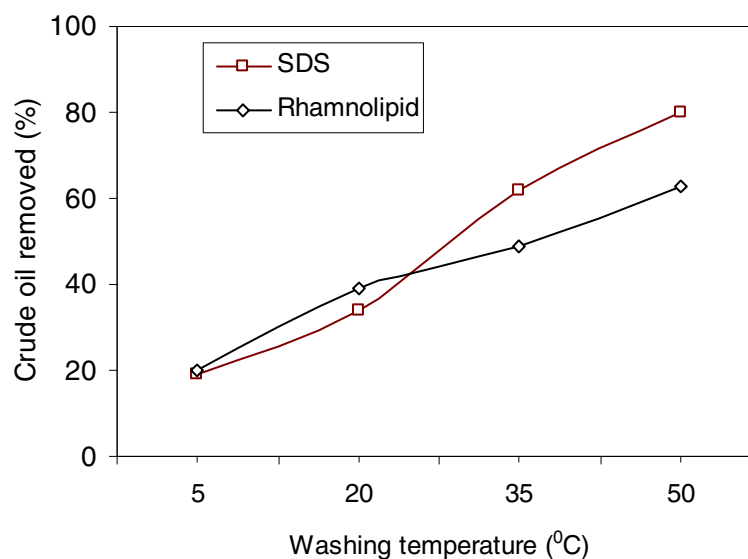


Figure 4.26. One-minute washing of the contaminated soil with 20 cm<sup>3</sup> 0.1%-mass solutions of rhamnolipid and SDS, shaken at 200 strokes/minute.

The results shown in Figure 4.26 indicate that during sixty seconds washing, crude oil removal at 5 and 20°C was about 20 and 40% respectively. Comparing this with Figure 4.21, at 5°C crude oil removal was about 10% for rhamnolipid and 25% for SDS but at 20°C crude oil removal was about 80%. Thus, at 5°C, increasing washing time did not enhance the crude oil removal, because of the correlation between temperature and viscosity. At low temperatures the washing solutions may not penetrate the interface between oil and soil interface. However, the twenty minutes washing result in Figure 4.21 showed that crude oil removal at 20°C was approximately the same as the oil removal at 50°C during the sixty seconds washing. As Figure 4.26 showed a linear relationship as temperature increases, this study suggested that washing for less than 10 minutes might save cost and time.

#### 4.2.1.7 Effect of pH adjustment on biosurfactants

To understand if the pH of surfactant solutions will contribute to greater crude oil removal, the natural pH of 0.1%-mass solutions of saponin, tannin and aescin was adjusted from 4.24, 3.60 and 3.80 respectively to 8 by adding 0.01 M NaOH solution.



The natural pH of saponin, tannin and aescin were less than that of rhamnolipid and SDS, which showed greater crude oil removal at their natural pH of about 7. Therefore, the new solutions of saponin, tannin and aescin were used to wash the contaminated soil by observing the effect of temperature, which shows more than 50% crude oil removal as parameter level increased in Figure 4.21.

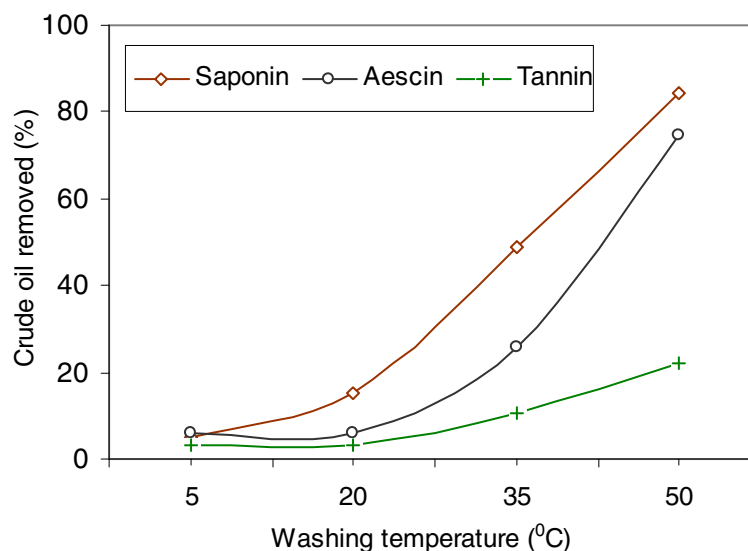


Figure 4.27. Crude oil removal with adjusted pH of 20 cm<sup>3</sup> 0.1%-mass solution. Washed for 20 minutes at shaking speed of 200 strokes/minute.

The results of this study are shown in Figure 4.27. Contrasting Figure 4.21 and Figure 4.27, the adjusted pH solutions of saponin and aescin showed a crude oil removal within the same experimental repeatability range. Tannin showed a reduction in crude oil removal at 35°C and 50°C but removal between 5°C and 20°C was still maintained at the experimental repeatability range. However, similar studies by Somasundaran et al. (1997) and Zhang et al. (2001) have suggested that elevating the pH of slurry of SDS/soil system from its natural pH of 6.5 to about 9 and 11 does not significantly enhance the removal of oil from soil. Therefore, Figure 4.27 suggests that pH adjustment may not be effective in enhancing crude oil removal from soil. The biosurfactants showed better removal of crude oil from soil at their natural pH at the given concentration.

#### 4.2.1.8 Blending of surfactant solutions

Considering the levels of parameters tested during the screening of surfactant solutions, it was observed that crude oil removal by most of the biosurfactant solutions was less than 50% (Figure 4.22 to Figure 4.25). Another test was carried out to investigate the enhancement of crude oil removal, when blended together 0.1%-mass solutions of rhamnolipid with each of the other surfactant solutions at different percentages. The results shown in Figure 4.28 indicated that at zero percent rhamnolipid solution, SDS removed more than 90% crude oil while tannin and lecithin removed about 10%, saponin and aescin removed less than 45% and distilled water about 40%. This study compares and confirmed the crude oil removal of the biosurfactants during the screening study.

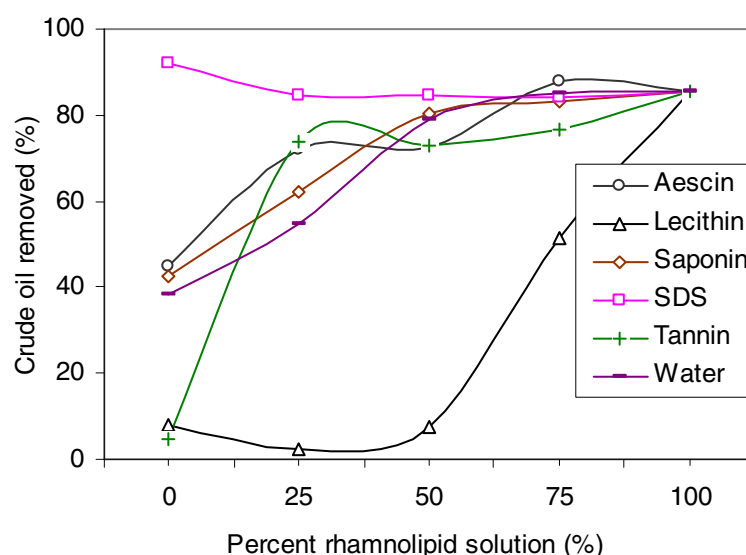


Figure 4.28. Crude oil removal of blending 20 cm<sup>3</sup> 0.1%-mass rhamnolipid solution with other surfactants at 20°C, shaken at 200 strokes/minute for 20 minutes.

As the rhamnolipid solution increased from 0 to 100 % blending ratio, the removal of crude oil by the biosurfactants and water was enhanced significantly except for lecithin which only showed increase with 75% rhamnolipid solution. Therefore, the performance of rhamnolipid was not affected by the other biosurfactant solutions in removing crude oil from soil, but it improved their performance as the blending percentage increased. Through this study lecithin was observed not to be effective in removing crude oil from soil at its natural state and with mixtures of rhamnolipid

solution. Lecithin solution was observed to be more viscous than the other solutions, which may hinder the penetration at the interface of oil and soil. Thus, it was not considered for further studies.

#### ***4.2.1.9 Scanning Electron Microscope***

To confirm the effect of surfactant solutions washing of the contaminated soil at different concentrations, a Scanning Electron Microscope (SEM) study was conducted on the washed soil samples to investigate the extent of crude oil removal. This study further showed better understanding on how the surface structure of soil grains changed with respect to appearance of troughs, grooves and cavities at different concentrations of surfactant solutions. The surface structure of soil grains can influence the removal of oil or retention of oil within the soil mass. Figure 4.29 shows the picture of the soil grain before contamination. This picture shows the evidences of grooves, cavities and ridges. This physical surface roughness will contribute in retaining crude oil within the soil mass, which may make oil removal difficult. Figure 4.30 shows the pictures of the non-weathered and weathered contaminated soil grain now covered by crude oil.

Analysis of these soil grains after washing with rhamnolipid indicated that, as the solution concentration increases from 0.004 to 0.5%-mass, the appearance of the soil surface roughness becomes clear and the cloud formed on the surface of the soil grains reduces significantly suggesting less oil on the soil (Figure 4.31 to Figure 4.34). A metal such as gold was used to spot on the soil surface, then SEM beam fires electrons at the soil surface. If the metal cannot spot the soil surface, the contaminated soil will “charge” negatively. This negative charge is seen as a “white” cloud in the pictures, it does not give any information about the surface structure of the soil.

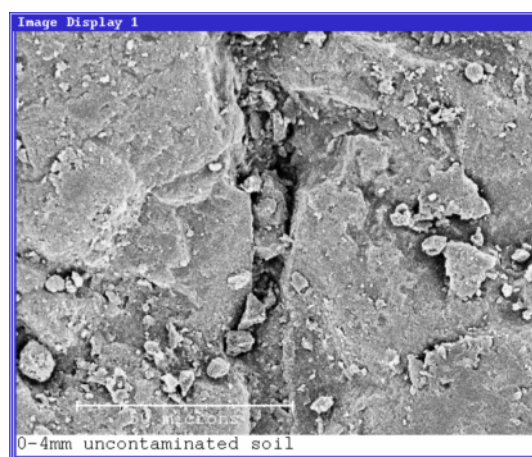


Figure 4.29. Soil – 4 prior to contamination with crude oil

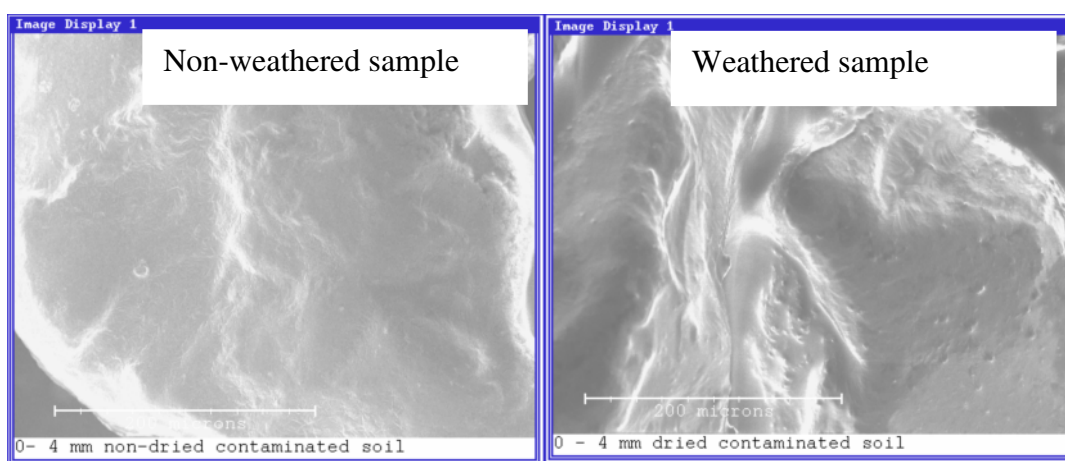


Figure 4.30. Soil – 4 contaminated with crude oil

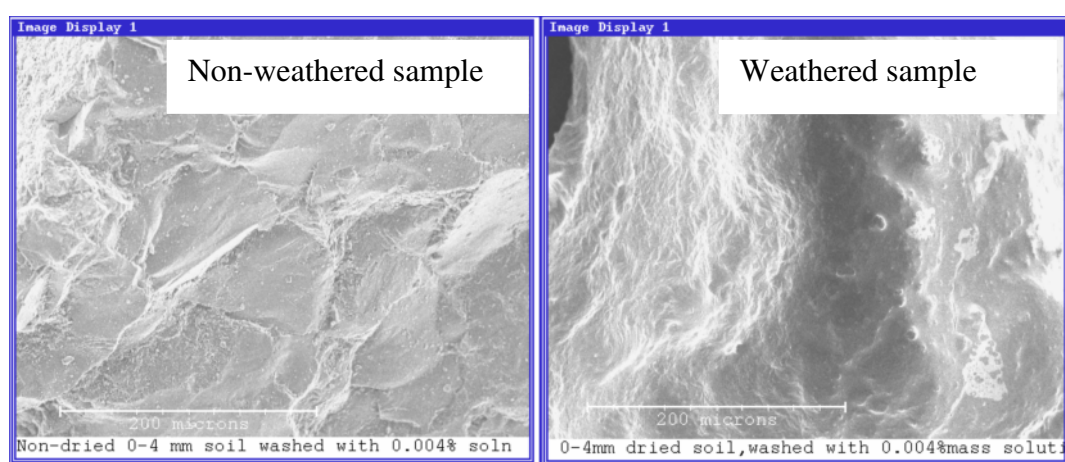


Figure 4.31. Soil – 4 washed with 20 cm<sup>3</sup> 0.004%-mass solution of rhamnolipid at 20°C, shaken at 200 strokes/minute for 20 minutes.

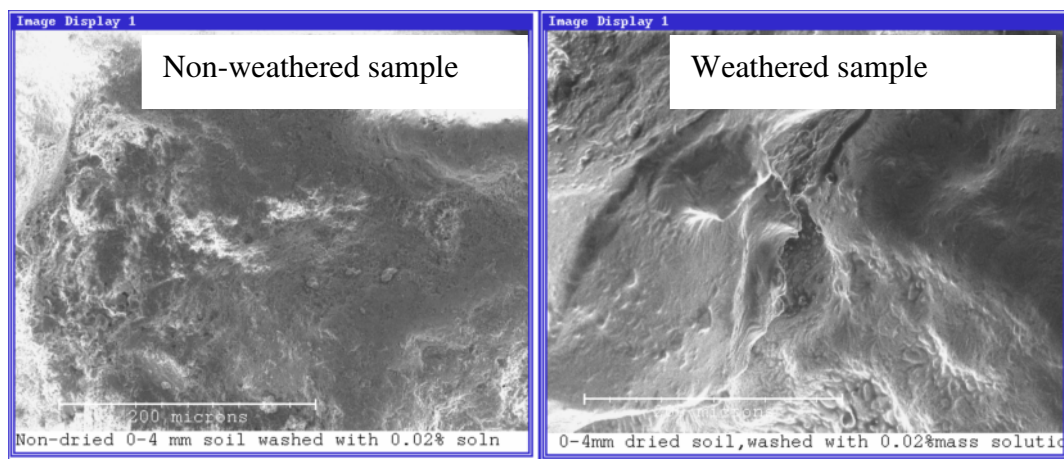


Figure 4.32. Soil – 4 washed with  $20 \text{ cm}^3$  0.02%-mass solution of rhamnolipid at  $20^\circ\text{C}$ , shaken at 200 strokes/minute for 20 minutes.

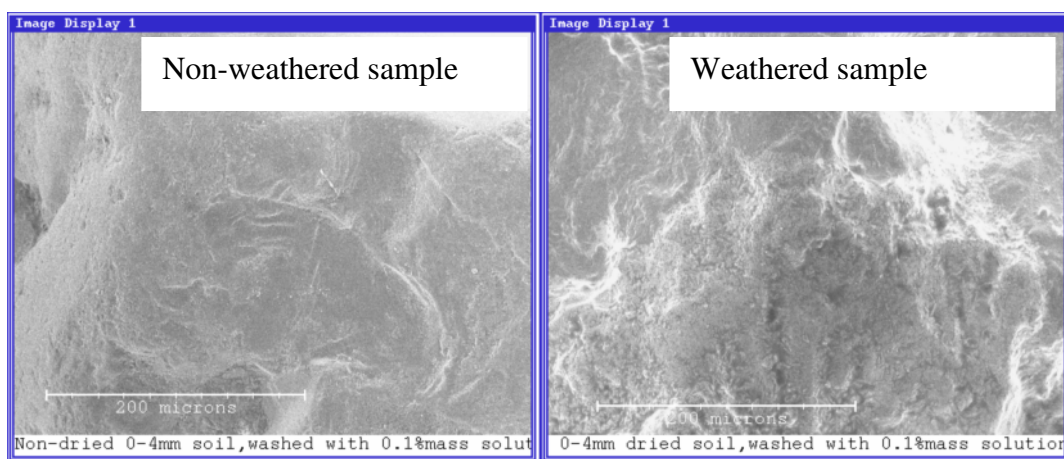


Figure 4.33. Soil – 4 washed with  $20 \text{ cm}^3$  0.1%-mass solution of rhamnolipid at  $20^\circ\text{C}$ , shaken at 200 strokes/minute for 20 minutes.

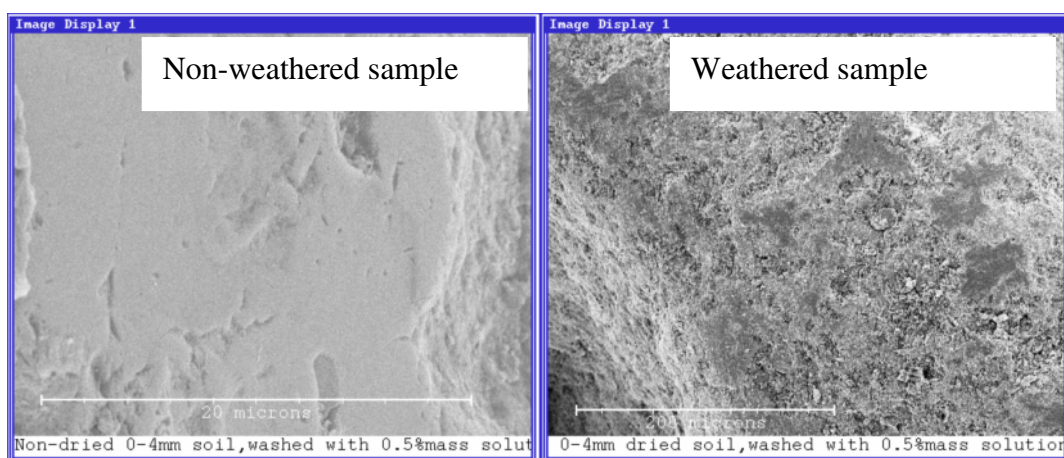


Figure 4.34. Soil – 4 washed with  $20 \text{ cm}^3$  0.5%-mass solution of rhamnolipid at  $20^\circ\text{C}$ , shaken at 200 strokes/minute for 20 minutes.

#### ***4.2.1.10 Conclusions***

Studies on biosurfactants removal of Ekofisk crude oil from laboratory-contaminated soils have been demonstrated through soil washing process. The following conclusions can be drawn from this study.

- Rhamnolipid and SDS were effective in removing up to 80% oil from the contaminated soil over the range of parameters tested. In most cases, rhamnolipid and SDS oil removal was within the same experimental repeatability range of  $\pm 6\%$ .
- Maximum crude oil removal was achieved at 50<sup>0</sup>C for all the surfactant solutions except lecithin that had a maximum removal of only 42% at 0.004%-mass solution.
- Apart from rhamnolipid, the performance of washing with water alone was equally good as those of the other biosurfactant solutions during blending. The approach of blending may be cost effective.
- The effect of washing temperature showed a significant removal of crude oil, more so than shaking speed, volume and concentration of surfactant solutions, and washing time. The effect of washing time however was less influential in crude oil removal because most biosurfactant solutions showed differences in crude oil removal of 30% between the first and fourth parameter levels.
- Therefore the results obtained through this study were used in designing a soil washing process for weathered crude oil contaminated soils in tests.

#### **4.2.2 Washing of different soil fractions**

In order to represent real-life conditions more accurately, different soil samples were chosen and all the contaminated soils weathered in a fan assisted oven at 50°C for 14 days. Rhamnolipid (R) and sodium dodecyl sulfate (SDS) were employed for this study. This is because their performance in removing crude oil from the non-weathered sample of Soil – 4 was observed to be more than 50% over the tested parameters whereas those of the other biosurfactants were not effective in Section 4.2.1. Therefore the other biosurfactants were not considered for this test which involved washing of weathered contaminated soil samples.

The weathered contaminated soil of Soil – 4 and three other soil samples namely Soil – 2, Soil – 3 and Soil – 5 were introduced in this section. The different soil fractions were studied due to their varying physiochemical characteristics such as pH, cation exchange capacity, surfactant sorption to soil, and crude oil content noted in Sections 3.2, 3.2.2 and 3.2.4. This study will be useful in assessing the performance of surfactants in washing different kinds of oil-contaminated soils that may be encountered in nature.

##### ***4.2.2.1 Effect of concentration of surfactant solutions***

The control (distilled water, W) washing showed a crude oil removal of about 5% from the weathered soil (w) samples of Soil – 2 and Soil – 3, and about 18% for Soil – 4 and Soil – 5. However, for the non-weathered (n) samples of Soil – 2 and Soil – 3, crude oil removal of 55 and 60% was achieved. Using surfactant solutions, crude oil removal was enhanced beyond the critical micelle concentration of 0.02 and 0.2%-mass for rhamnolipid (R) and SDS respectively. As the concentration of the surfactant solutions increases the overall performance of rhamnolipid and SDS in removing crude oil from the weathered soil samples were in the following order: Soil – 5 > Soil – 4 > Soil – 3 > Soil – 2.

Crude oil removal from the weathered and non-weathered soil samples (Figure 4.35) increased as the concentration of surfactant solutions increased. The low removal of crude oil from the weathered soil samples was a result of the complex nature of the oil, due to loss of volatile components during weathering. The weathered contaminated



soils reduce the interaction and penetration of the surfactant solutions at the interfaces between crude oil and soil, therefore reducing the crude oil removal efficiency with surfactant solutions.

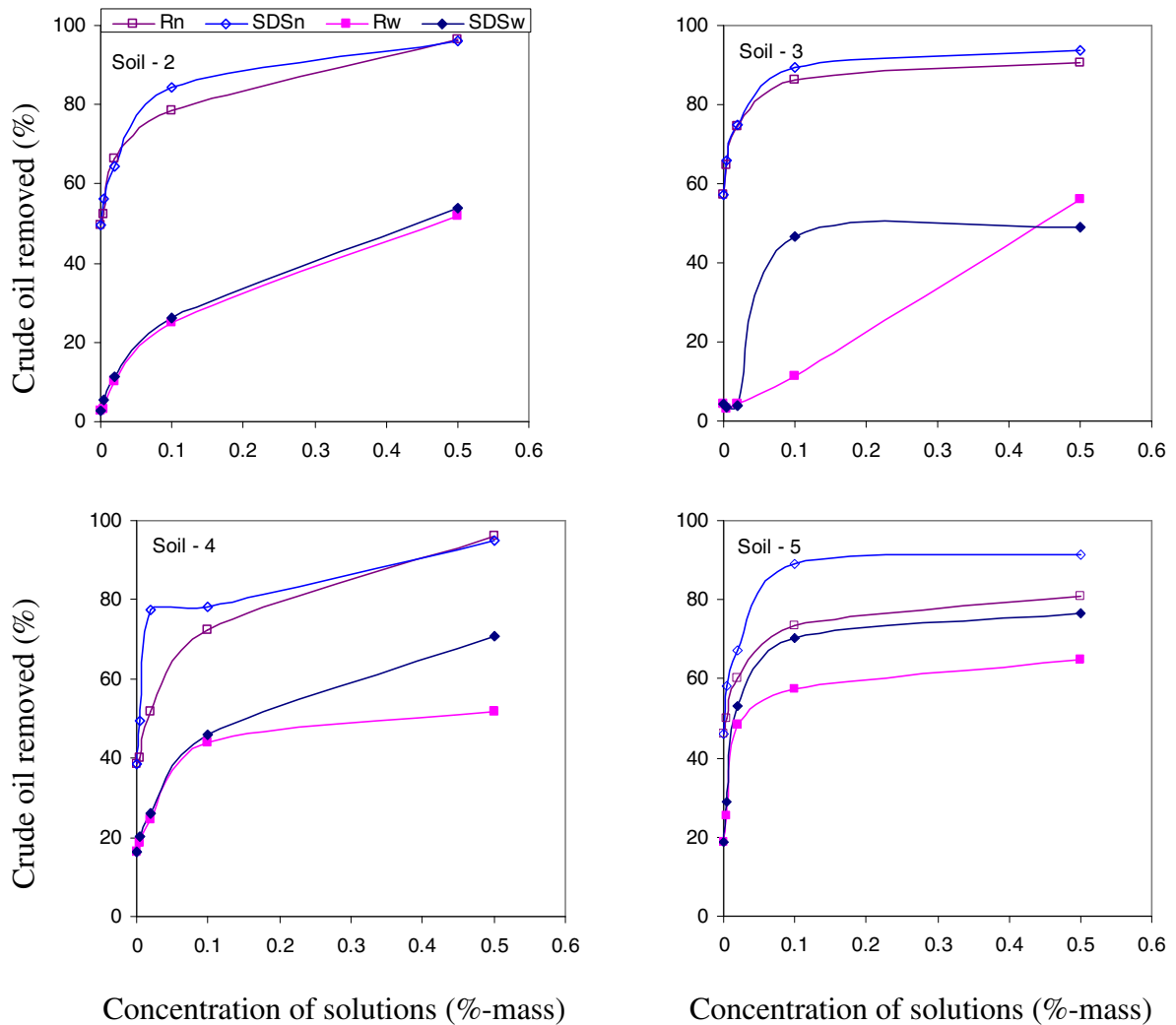


Figure 4.35. Crude oil removal from the weathered and non-weathered soil samples as function of concentration of surfactant solutions (washed at 20°C with 20 cm<sup>3</sup> solution, shaken at 200 strokes/minute for 20 minutes).

Generally, Rn and SDSn can be approximated within the repeatability range of  $\pm 6\%$ , except for Soil – 5 that indicated about 10 % more oil removal in favour of SDS. As the soil particle sizes increased and the concentration of solutions increased, crude oil removal from the weathered and non-weathered soil samples appeared to respond similarly. This study was comparable with Harvey et al. (1990) in Figure 4.36, which suggests that the desorption of crude oil from soil with aqueous surfactant solutions may be effective in treating soils with larger particle sizes than the finer (Soil - 2) ones.



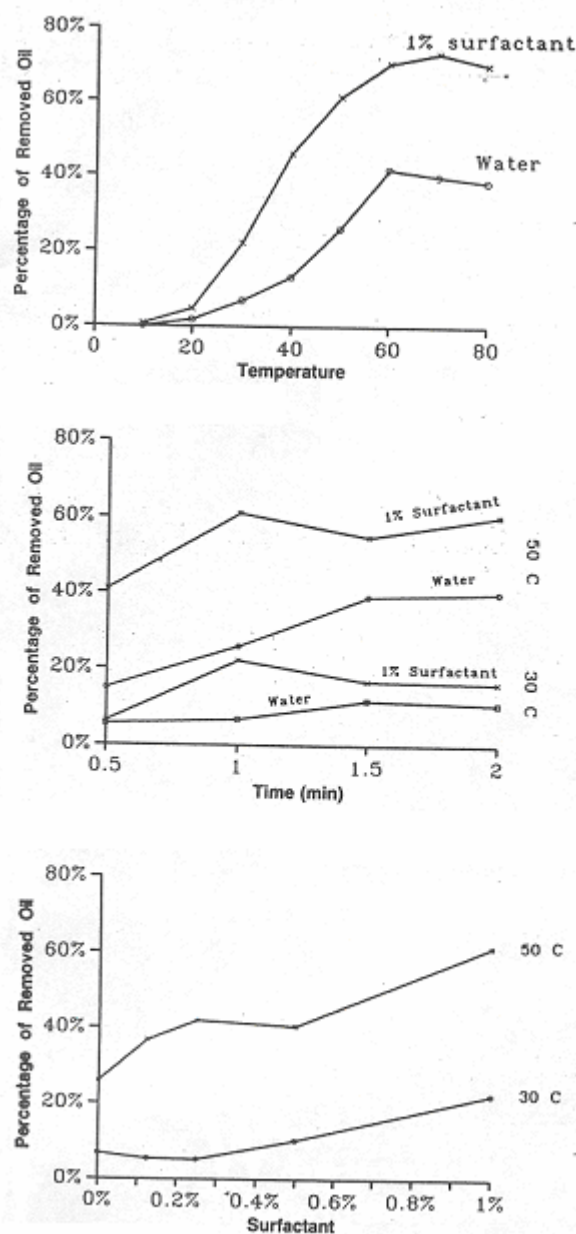


Figure 4.36. The removal of spilled crude oil from Alaskan gravels using a microbial surfactant. Adopted from Harvey et al. (1990).

The greater crude oil removal from Soil – 5 (with 100 % gravel) may be due to the lower oil content, neutral pH and CEC. Higher CEC indicates greater organic matter content in soil and high pH as noticed with Soil – 3 and Soil - 4. Soil pH affects CEC, the soil has an exchange site that becomes active as the pH increases. Soil-2 showed the lowest pH of 6.29 (Section 3.2.1.6). Its CEC was expected to be higher than 7.58 *meq/100g* soil because the soil has larger surface area and thus more sites readily

exchangeable in comparison to Soil – 3 and Soil – 4 which both demonstrate CEC of 14.32 and 10.17 *meq*/100g soil respectively. Clay and organic matters in the soil have negative charges, so naturally attracts positively charged ions and repels negatively charged ions. Therefore, this may also lead to stronger binding of the oil with the finer soil samples (Soil – 2).

#### ***4.2.2.2 Effect of temperature***

The results of the effect of washing temperature in Figure 4.37 shows variation in crude oil removal for all the soil fractions, as the washing temperature increased. The trend in oil removal was similar for the different washing solutions in each of the soil samples; it follows that increase in temperature will reduce the crude oil viscosity thereby increasing the oil mobility and interaction with surfactant solution. For most of the non-weathered samples, SDS and rhamnolipid had a constant crude oil removal above 20<sup>0</sup>C whereas the weathered samples indicated that more crude oil could be removed if temperature was increased beyond 50<sup>0</sup>C.

At 50<sup>0</sup>C, crude oil removal from the non-weathered soil samples was twice that of the weathered samples, with Soil - 4 and Soil – 5 showing constant oil removal above 20<sup>0</sup>C. Therefore, crude oil removal from the weathered soil samples was enhanced for soil with large fractions (Soil – 5). The large soil fractions have less initial crude oil content, therefore their crude oil removal in 20 minutes may be faster compared to the finer soil samples. Since the non-weathered soil samples were freshly contaminated, crude oil removal from the finer soils (Soil – 2 and Soil - 3) was enhanced. This is because of their large surface area and less oil retention in their pores thereby encouraging the surfactant solution penetrating the soil-oil interface.

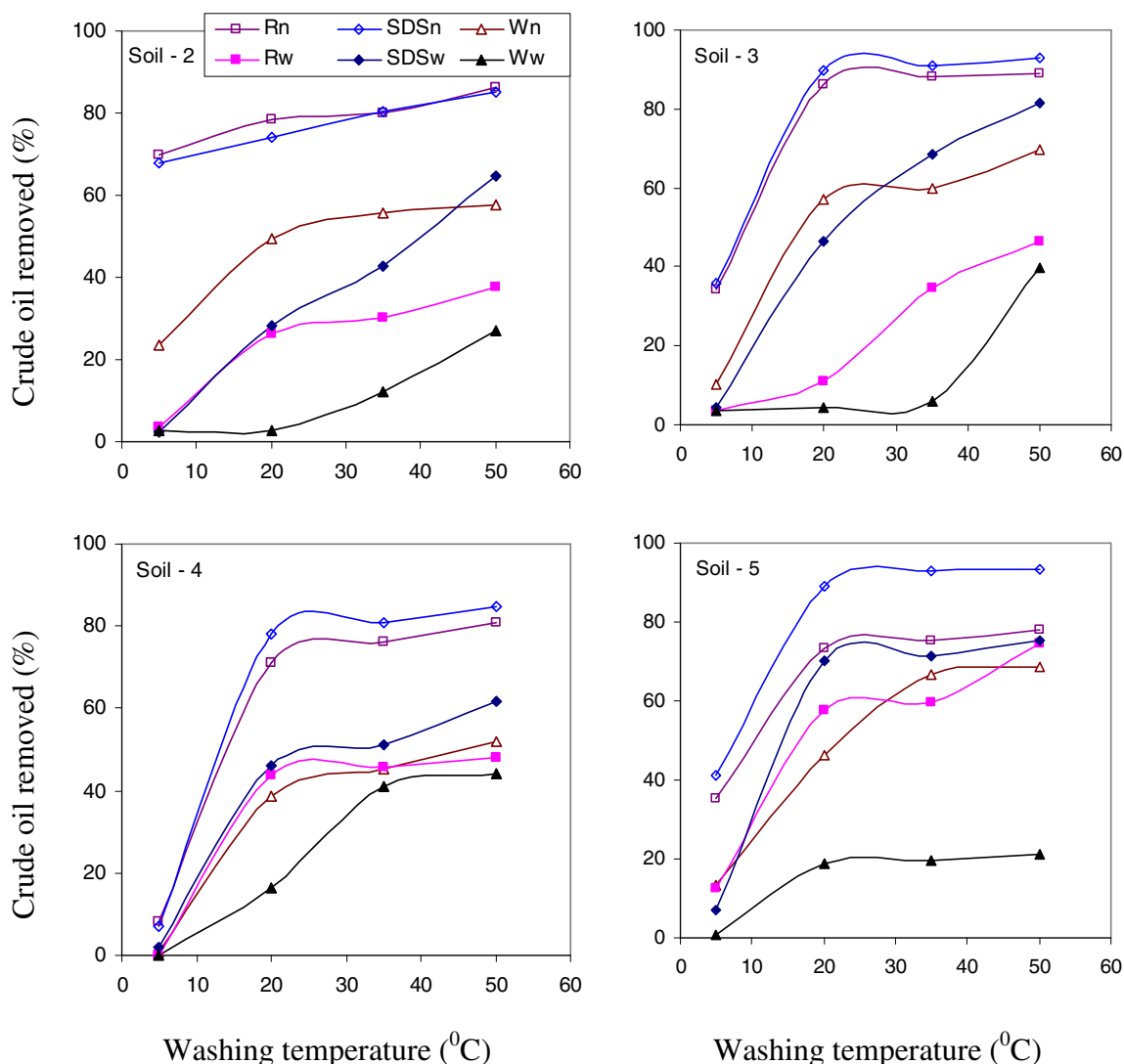


Figure 4.37. Crude oil removal from weathered and non-weathered soil samples versus as function of washing temperature (washed with 20 cm<sup>3</sup> 0.1 %-mass solution, shaken at 200 strokes/minute for 20 minutes).

#### 4.2.2.3 Effect of solution volume

To facilitate the crude oil removal, the interaction of surfactant in the interface between crude oil and soil was investigated by varying the volume of washing solutions from 5 to 20 cm<sup>3</sup>. The increase in volume of surfactant solutions shows a corresponding increase in crude oil removal using rhamnolipid and SDS (Figure 4.38). Therefore, increase in volume enhances the interaction between the crude oil and washing media. In some cases with distilled water, crude oil removal from the weathered soil samples was observed to be constant indicating the non-influence of change in volume after a

certain level. The weathered soil samples of Soil – 4 and Soil – 5 also showed a crude oil removal of about 18 and 10% respectively, after 15 cm<sup>3</sup>. Therefore, the plots (Ww and Wn) in Soil - 5 agree with the work of Anderson et al. (1999), that water based soil washing is recommended for soil with particle size greater than 2 mm.

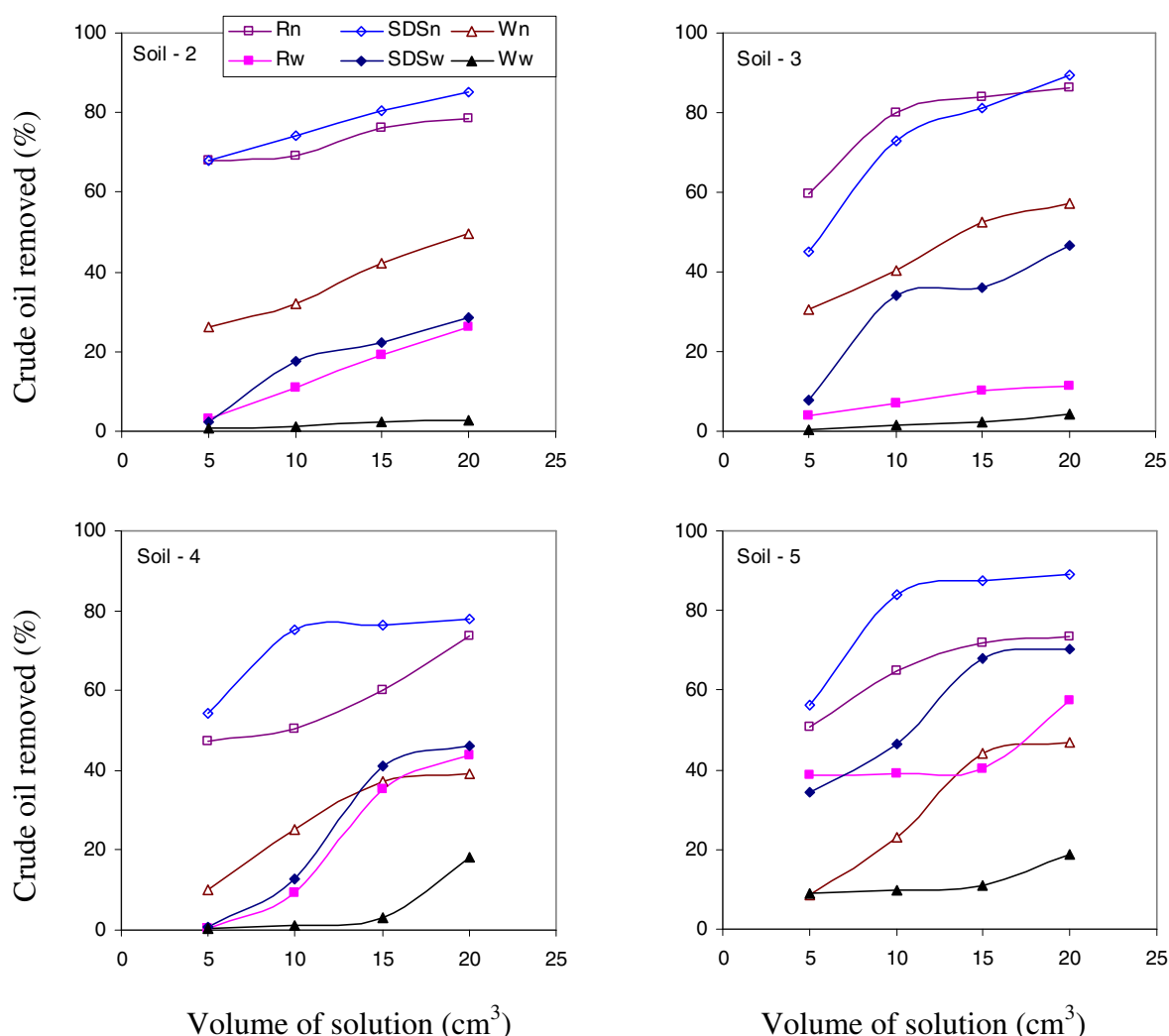


Figure 4.38. Crude oil removal from the weathered and non-weathered soil samples as function of volume of washing solution (washed at 20°C with 0.1 %-mass solution, shaken at 200 strokes/minute for 20 minutes).

#### 4.2.2.4 Effect of shaking speed

The results of this study indicated that an increase in shaking speed enhanced the removal of oil as shown in Figure 4.39. The plots (Rn, SDSn, and Wn) showed significant crude oil removal over the range of shaking speed (80 to 200 strokes/minute) tested. As shaking speed increases, more surface area of the contaminated soil is

exposed to the surfactant solution, thus the surfactant solution displaces the crude oil from soil. Rn and SDSn showed a removal within the same repeatability range of  $\pm 6\%$ . The overall crude oil removal from the weathered soil sample was in the following order of soils: Soil – 5 > Soil – 4 > Soil > 3 and Soil > 2. Zhang et al. (2001) and Somasundaran et al. (1997) have attributed the enhanced oil removal as a result of the displacement of oil by surfactant solutions, which was due to the scrubbing of contaminated soil surfaces that generates attrition and abrasion.

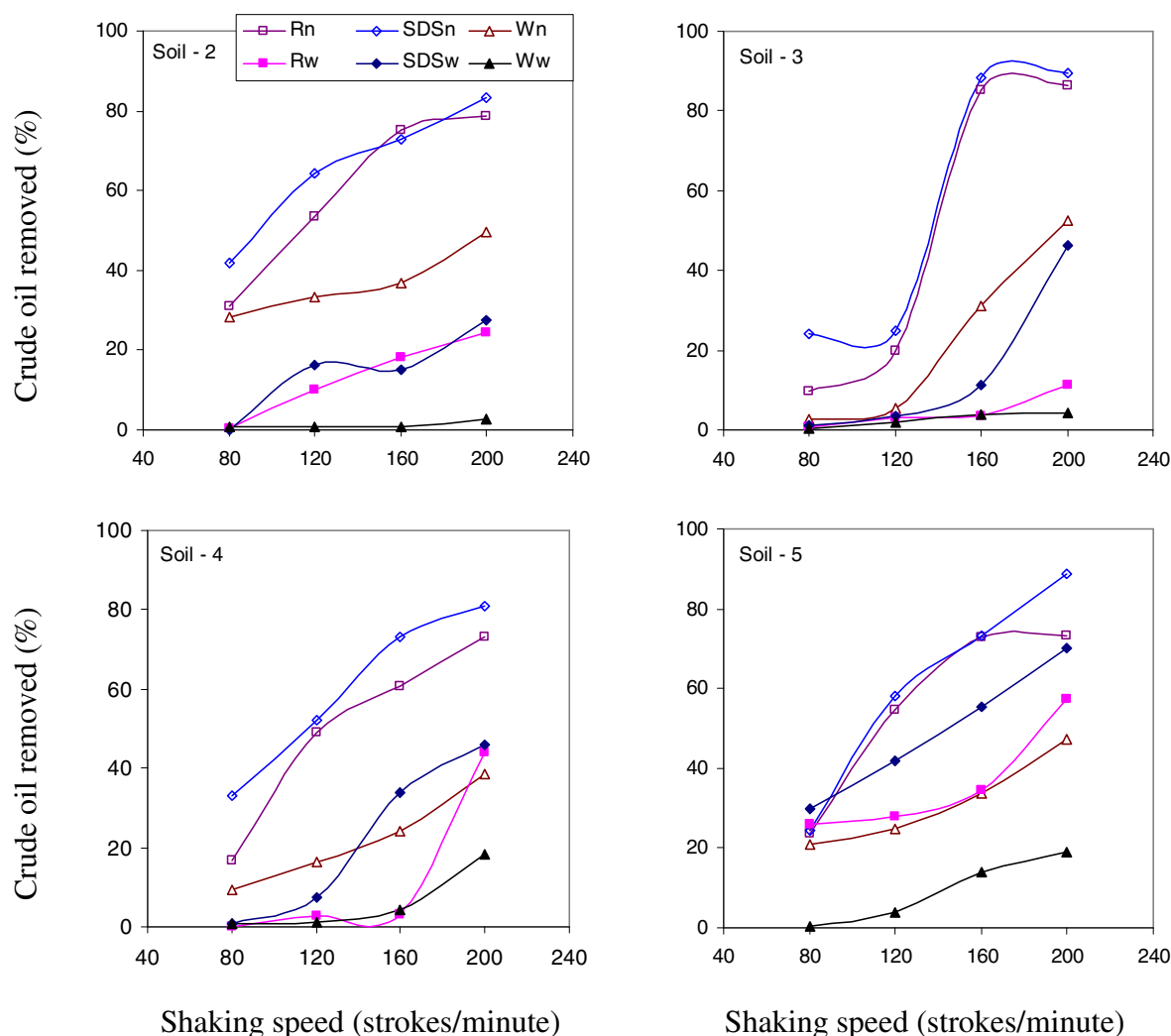


Figure 4.39. Crude oil removal from weathered and non-weathered soil samples as function of shaking speed (washed at  $20^{\circ}\text{C}$  with  $20\text{ cm}^3$  0.1 %-mass solution for 20 minutes).

#### 4.2.2.5 Effect of washing time

Increase in washing time leads to an increase in crude oil removal for both the weathered and non-weathered soil samples, as shown in Figure 4.40. Crude oil removal

from the weathered soil samples improved as the soil particle size fraction increased. However, the reverse was true for the non-weathered soil samples. The enhancement may be due to the least oil content with the larger soil fractions.

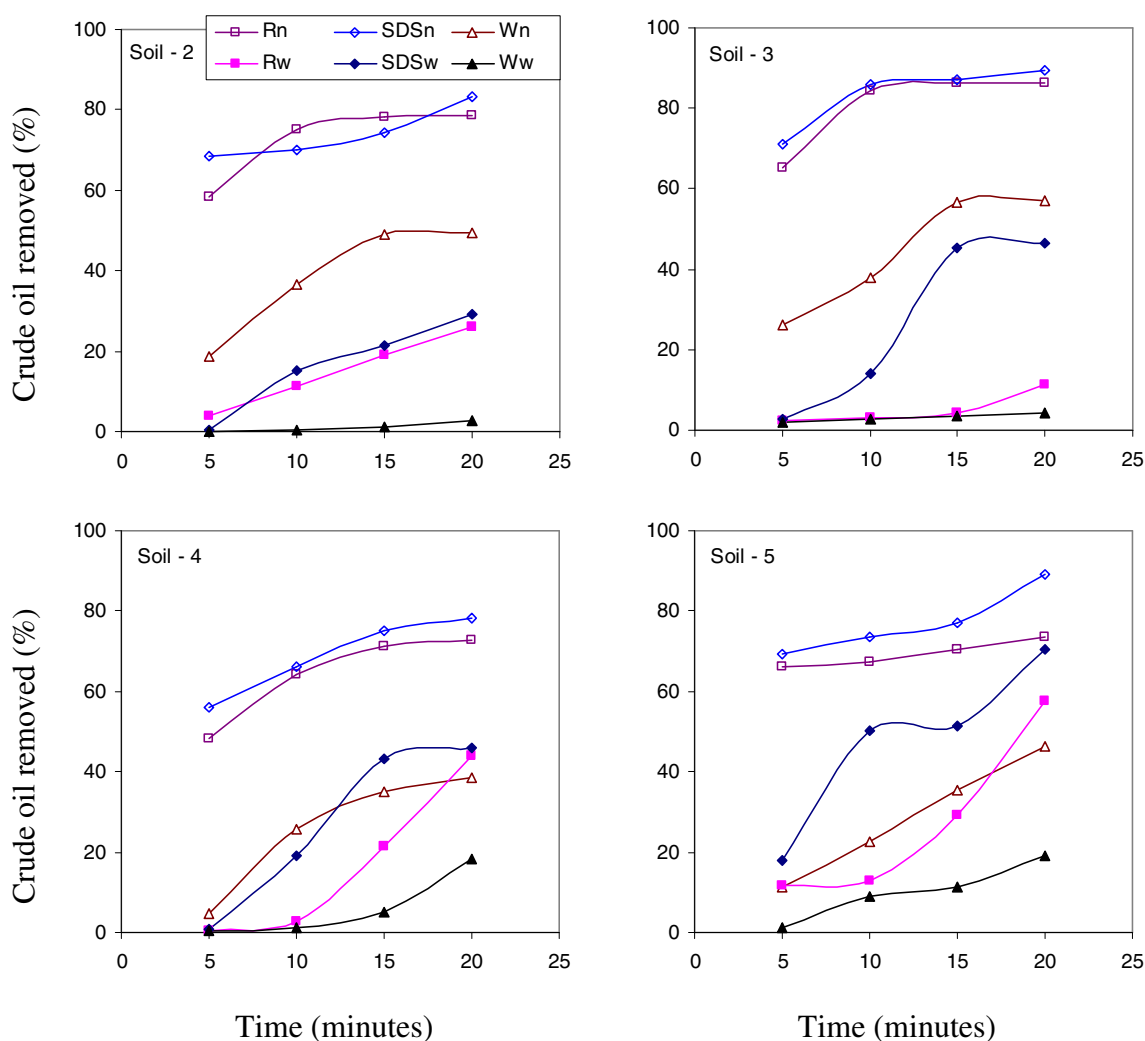


Figure 4.40. Crude oil removal from the weathered and non-weathered soil samples as function of washing time (washed with 20 cm<sup>3</sup> 0.1-% mass solution at 20<sup>0</sup>C shaken at 200 stroke/minute).

#### 4.2.2.6 Conclusions

Rhamnolipid, SDS and distilled water were employed in this study to remove crude oil from different weathered and non-weathered contaminated soil samples by investigating the effects of different parameters; washing temperature, volume and concentration of solutions, shaking speed and washing time. The following conclusions can be made from the study:

- Notwithstanding the differences in the physicochemical properties of surfactant solutions such as sorption to soil, solubilization, surface and interfacial tension, the removal of crude oil from the weathered and non-weathered soil samples using rhamnolipid and SDS was within the same experimental repeatability range  $\pm 6\%$ .
- The surfactants enhancement of crude oil removal was better for the non-weathered soil than for the weathered soil samples. This was explained due to the resulting complex nature of the weathered contaminated soil that contained oil with higher molecular weight.
- The overall crude oil removal from the non-weathered soil samples were in the following descending order: Soil – 2 ( $< 0.06$  mm), Soil – 3 ( $< 2$  mm), Soil – 4 ( $< 4$  mm) and Soil – 5 (2 - 4 mm), whereas the reverse was true for the weathered samples. This was possible since the non-weathered soil samples are freshly contaminated thus, the binding of oil to soil will be less, coupled with the large surface area of the fine samples. For the weathered samples, the oil content in soil fractions was less with larger soil fractions therefore fast desorption of oil from soil will be expected.
- The results obtained throughout this study could be generalized for other non-aqueous phase liquids. The data obtained through this study was used to design a stirred tank and column mode soil washing processes and presented in subsequent chapters of this thesis.

### **4.3 Soil washing with stirred tank reactors**

Soil washing in stirred tank reactor was examined to mimic the ex situ soil washing technique in Deshpande et al. (1999), Feng et al. (2001) and Krishnan et al. (1996). This study employed two contaminants (crude oil and heavy oil) and the amount of contaminated soil washed with rhamnolipid saponin and SDS prepared in either distilled water or seawater was scale up to 10g. The biosurfactants (saponin and rhamnolipid) were chosen because they showed better crude oil removal in Section 4.2 and literature on SDS characteristics with petroleum hydrocarbon is well studied by Deshpande et al. (1999), Rosen (1989), Elvers et al. (1994), Holmberg (2002) and Lake (1989). Heavy oil was investigated, because:

- Its removal from soil using surfactant solutions is also known by Liu et al. (1995) and Cheah et al. (1998).
- It shows different physical properties, most significantly viscosity and density, than Ekofisk crude oil, which is a light oil.

With emphasis on crude oil, the oil removal from the different soil fractions (Soil – 1, Soil – 3, Soil – 4 and Soil – 5) employed in this study were used to simulate the effect of the range of soil particle sizes found naturally. In this section, Soil – 1 replaces Soil – 2, Soil – 2 as presented in Section 4.2.2 had the fine soil particles, low pH and low CEC, but did not show better crude oil removal compared to the other soil fractions, therefore Soil – 1 was introduced. Soil – 1 has finer particles and can simulate drilling mud or drilling cuttings that is generated as waste during crude oil drilling operations.

Due to limited literature in this area of study, results obtained are compared with SDS. The applicability of this study would not only rely on the treatment of soils contaminated by petroleum oil spills, but in managing contaminated soils generated through drilling operations that are improperly disposed.

The results of the effects of the different parameters tested are presented in the subsequent sections of this chapter.

#### **4.3.1 Effect of surfactant concentrations**

The effect of surfactant concentration on oil removal was investigated in the range of



zero %-mass (distilled water) to 0.5 %-mass and the results are presented in Figure 4.41. The experimental conditions for this set of data were washing temperature (20<sup>0</sup>C), ratio of volume of surfactant solution to mass of crude oil (30 cm<sup>3</sup>/g), stirring speed (480rpm) and washing time (10 minutes). Critical examination of the results indicates that all the surfactants show the same trend in oil removal from the different soil samples. In Soil – 1 plots, the surfactant solutions shows approximately constant oil removal of more than 95%. The figure further depicts that crude oil removal from the weathered soil sample is enhanced by surfactant solutions from about 50% (using distilled water) to 90% with 0.1%-mass solutions. The disparity of more than 40% crude oil and heavy oil removal from Soil – 1 using water alone and 0.02 %-mass solutions may be due to the resulting nature of crude oil after weathering (Section 3.1.3.1 and 3.1.4). It was discovered that during washing, the weathered samples of Soil – 1 do not mix with the surfactant solutions at lower parameter values (1<sup>st</sup> and 2<sup>nd</sup>), there was formation of distinct parts of contaminated soils. This behaviour with Soil – 1 with larger surface area, may be due to the reason of containing more complex unresolved materials. Disparity with less than 39% oil removal between crude oil and heavy oil however, was also noted from Soil – 3, Soil – 4 and Soil – 5.

All the soil samples have approximately the same neutral pH range as indicated in Section 3.1.1.7. The surface area per mass is in the decreasing order of Soil – 1, Soil – 3, Soil – 4 and Soil – 5. Soil with large surface area is advantageous and disadvantageous in oil removal. Soil - 1 has larger surface interactions with regards to oil therefore the removal of oil may be hindered since there is greater binding of oil and soil. However, oil/surfactant and oil/water systems will aid the oil removal process since more area of soil will be available for the surfactant to attack. Therefore the greater oil removal of more than 90% from the weathered and non-weathered samples may be attributed to the interaction of surfactant at the interface between soil and oil. This implied that the interaction of surfactant/soil system (such as sorption of surfactant to soil) and surfactant/oil system (such as interfacial tension reduction, solubilization and emulsifications) would dominate the interaction of oil/soil system.

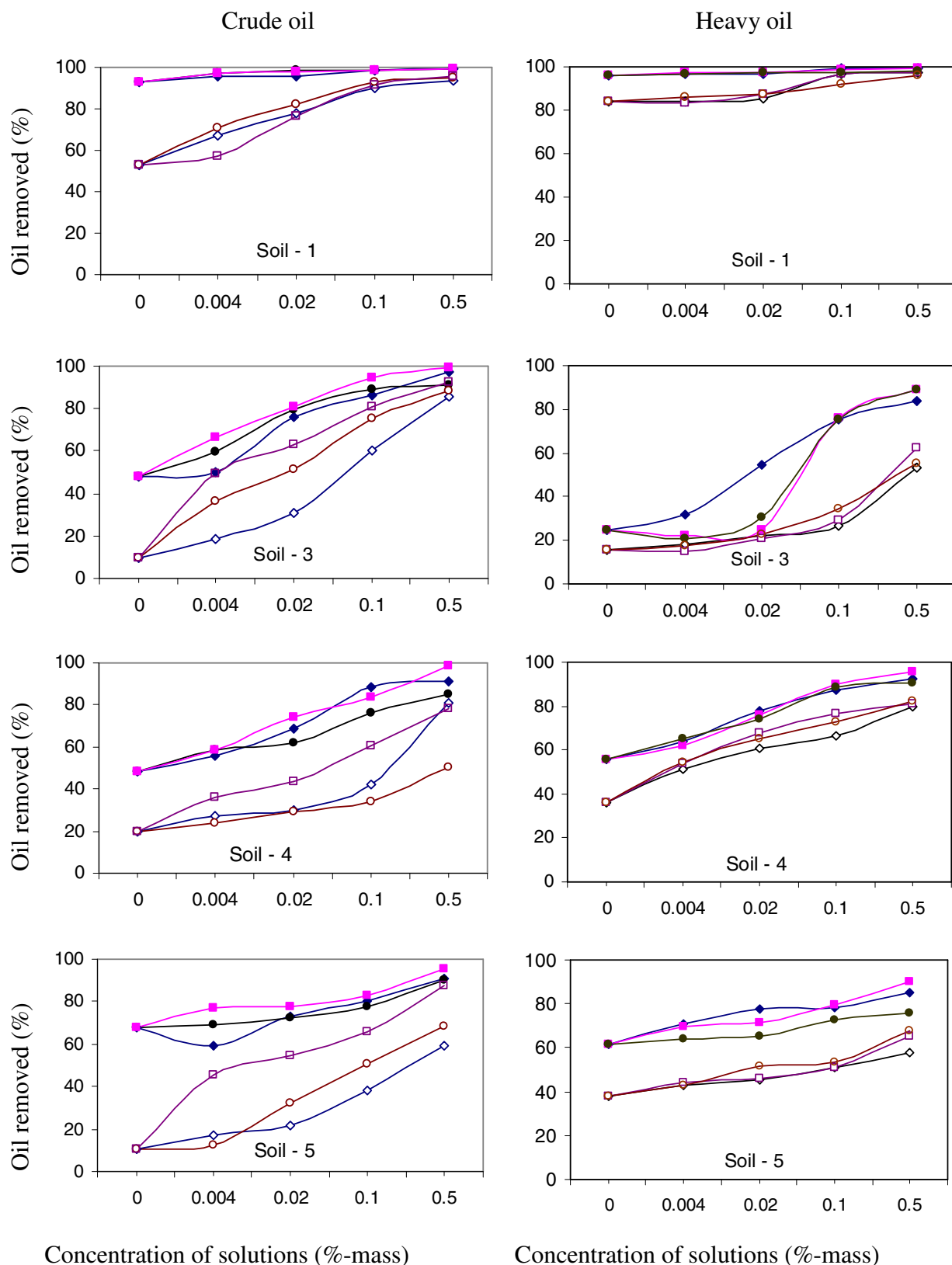


Figure 4.41. Oil removal as function of surfactant concentration (washed at 20°C and 480 rpm with 30cm<sup>3</sup> surfactant solution for 10 minutes).

With the large net negative surface charges and high CEC (44.75 meq/100g soil) associated with Soil – 1, the repulsion between the surfactant hydrophilic portions will be more than the other soil samples. These repulsions will lead to the enhancement of oil removal capacity of the surfactants without considering the differences in their ionic groups. Therefore, the sorption of surfactant to soil does not have any significant effect on oil removal from Soil –1 indicating that oil removal may be due to the reduction of interfacial tensions at the water-oil interface. However, for the other soil fractions, SDS with the least value of percent sorption to soil has better oil removal from the weathered contaminated soils. This indicates that the effect of soil sorption is important in applying this technology for weathered contaminated soils. Therefore, sorption to soil is a site-specific parameter that must be determined before treating weathered contaminated sites.

Oil removal from the weathered and the non-weathered samples of Soil – 3, Soil – 4 and Soil - 5 was observed to increase as surfactant concentration is increased. With the initial amount of oil in the soil (Section 3.1.3) and the low solubilization of crude oil (Section 4.1.6), it was thought that oil removal from soils is due to mobilisations as also noted in Section 2.5.1. The linear relationship between the surfactant concentrations and oil removal from the weathered soil samples suggest that more oil could be removed above the surfactants CMC where the micelles are readily available to partition on the crude oil.

Surfactants interfacial activities and micelle formation are influenced by the size and structure of the hydrophobic moiety. The hydrophobic moiety determines the cohesive forces between the surfactant molecules and ions as well as their behaviour at the interface. Since cohesive forces are increased with increasing hydrophobic chain length, and are stronger than the force that exist between branched alkyl chains, surfactant, with linear alkyl group form micelles at lower concentrations than those with branched chains while those with long chains form micelles at lower concentrations than those with short chains, Elvers et al. (1994). Due to the differences in the chemical structure of the surfactant solutions employed in this study, greater oil removal was expected from surfactants with low molecular weight with less bulky and complex hydrocarbon chains. In Section 3.1.5 saponin has the largest weight and more complex followed by rhamnolipid and then SDS. In most cases, oil removal was in the following descending

order: SDSn, Sn and/or Rn and SDSw, Sw and Rw. The order of oil removal appears to be the same as order of surfactant foaming stability (Section 4.1.3) and sorption to soil (Section 4.1.4).

Contrasting this study with that of the test tube in Section 4.2.2.1, crude oil removal from the non-weathered samples of Soil – 3, Soil – 4, and Soil – 5 can be assumed to be within the same range. For the weathered samples, the stirred tank study showed a greater enhancement in crude oil removal than in the test tube study even though the amount of the contaminants doubles that of the test tube. It is thought that the mechanical effect of the stirrer contributes to this increased oil removal. Detailed studies on the mechanical effect of the stirrer will be given in Section 4.3.3. Since the intensity of mixing resulted in a better interfacial contact of the surfactants and soil, this study further suggest that soil washing in stirred tank reactors is a good approach for the treatment of weathered contaminated soil. .

#### **4.3.2 Effect of temperature**

In the view of Holmberg (2002), temperature affects both the oil and washing solutions. Increase in temperature reduces oil viscosity, thereby increasing the mobility of the oil. Also increase in temperature reduces the surfactants' CMC and increased their surface activities. The results of the effect of washing temperature in Figure 4.42 show an upward trend in oil removal from 5 to 50<sup>0</sup>C. The removal of oil from Soil – 1 is similar to those obtained in Section 4.3.1 while a significant oil removal is observed in Soil – 3 between 5 and 20<sup>0</sup>C for all the washing media. Also, between 20 to 50<sup>0</sup>C, all the surfactant solutions performances were within the repeatability and error range of  $\pm 4\%$ . It is believed that increase in temperature, increases the solubility of anionic surfactant and decreases those of the non-ionic ones because the extent of hydration through hydrogen bond formation decreases with increasing temperature.

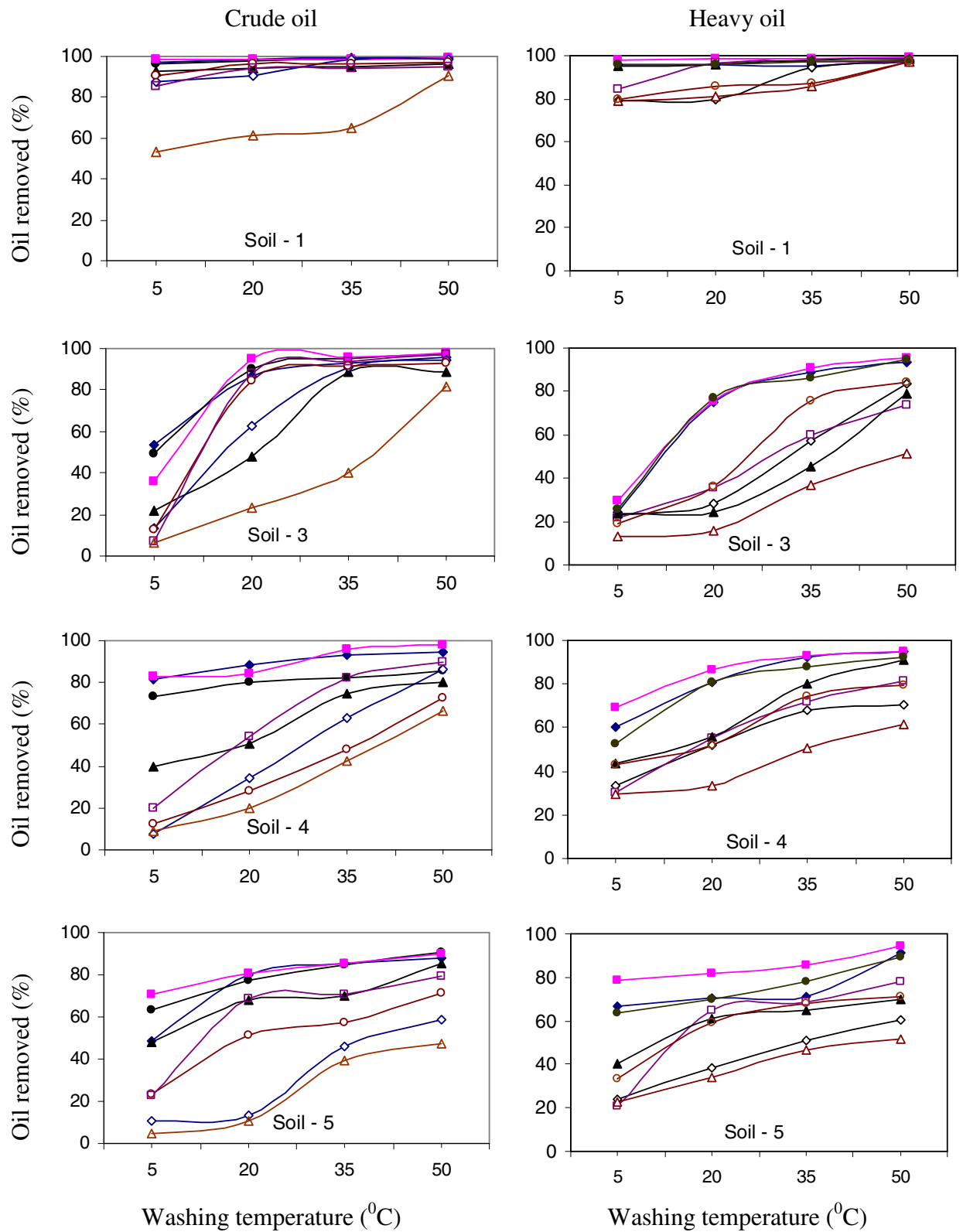


Figure 4.42. Oil removal as function of temperature (washed with  $30\text{ cm}^3$  0.1%-mass solution at 480 rpm for 10 minutes).

—◆— Rn —●— Sn —■— SDSn —▲— Wn —◇— Rw —○— Sw —□— SDSw —△— Ww

Generally the removal of oil from the non-weathered soil samples was better than the weathered samples. In most cases oil removal from the non-weathered soils showed a constant removal above 20 and 35<sup>0</sup>C. The disparities in oil removal from the two contamination cases (weathered and non-weathered) were more pronounced as the soil particle fraction is increasing. This lower oil removal from larger fractions of the weathered soil samples may be due to the reason of surface roughness of the soil, leading to the binding of oil to soils. As the soil samples have grooves and cavities (Section 4.2.1.9), the oil will stick inside these pores and thus, may reduce the surface interaction with the surfactants.

Distilled water showed a considerable oil removal tendency as the temperature is increased. The results of washing the weathered samples showed a linear relationship between oil removal and temperature suggesting that that more crude oil could be removed if temperature increased beyond 50<sup>0</sup>C. In such cases, the surface attractive forces are reduced thereby favouring the dispersion of contaminated soils. Such enhancement in oil removal could be regarded as mobilization due to the reduction of oil viscosity, which favours the interfacial contact of the oil with aqueous surfactant solutions.

#### **4.3.3 Effect of stirring speed**

The results of the effect stirring speed on oil removal from soils are presented in Figure 4.43. It can be seen that increase in stirring speed from 240 to 600 rpm improves oil removal from the soil samples except during the washing of the non-weathered samples of Soil – 1. Surfactants removal of oil from Soil – 1 have a constant value of 90% indicating that the speed of 240 rpm could disperse the soil into the surfactant solutions. The reasons behind the greater oil removal from Soil – 1 have already been explained in Section 4.3.1.

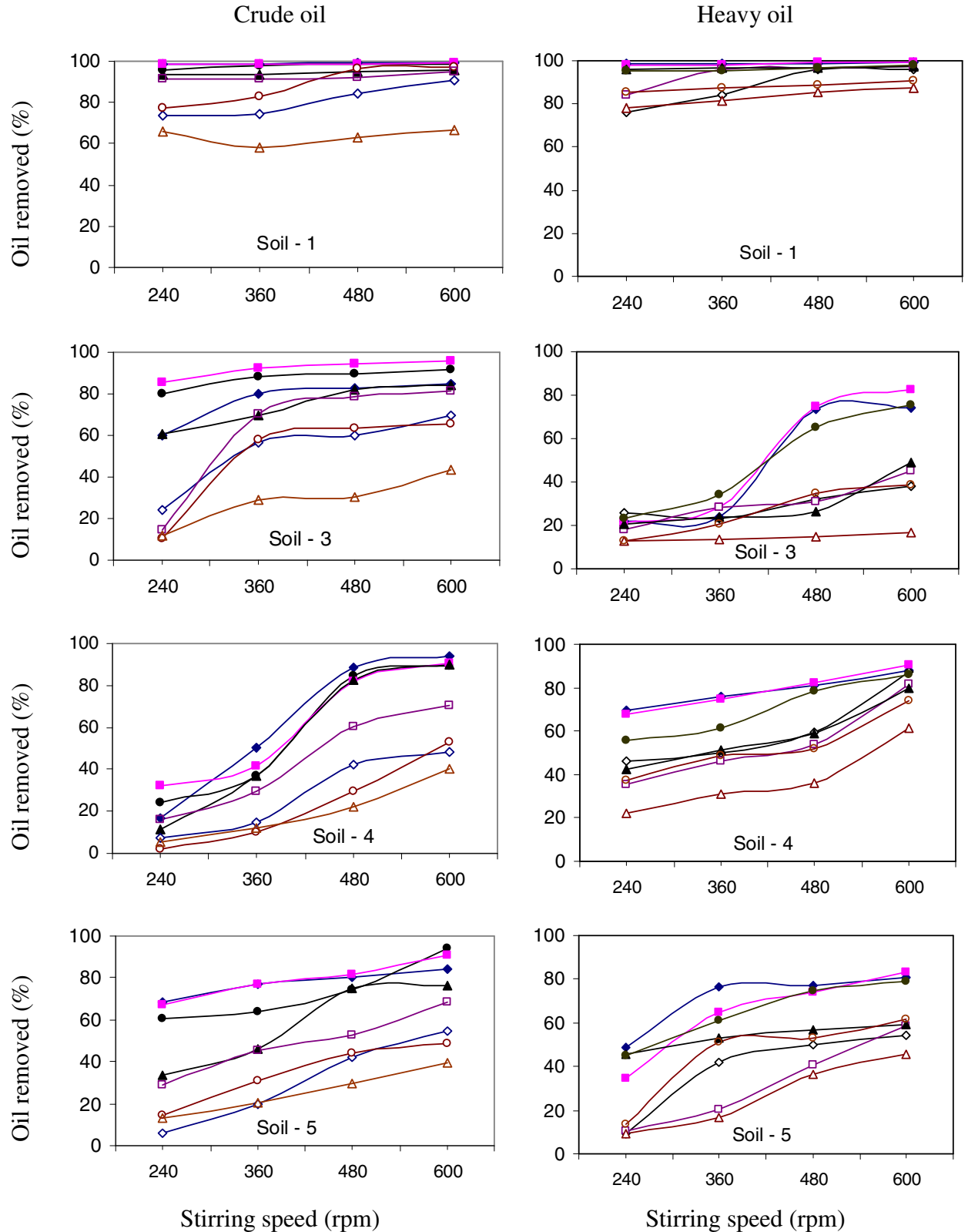


Figure 4.43. Oil removal as function of stirring speed (washed with  $30 \text{ cm}^3$  0.1%-mass solution at  $20^\circ\text{C}$  for 10 minutes).

With the large CEC of (44.75 *meq*/100g soil) associated with Soil – 1, the net negative sodium ions in the soil would act as an electrolyte, thereby creating electrostatic repulsion of the surfactant hydrophilic moiety groups and probably reduce the surfactant CMCs (Section 2.6). It could be argued that oil removal from the other soil samples will increase with soils that have greater CEC. However, critical examination of Figure 4.43 does not show this, therefore, the whole oil removal enhancement of surfactants relies on the scrubbing of the soil particles against each other.

As all the surfactants showed oil removal within the experimental repeatability range, it might be concluded that their performances are the same, even though they have different surface activities such sorption to soil. The oil removal from Soil – 3, Soil – 4 and Soil – 5 agrees with the study of Somasundaran et al. (1997), which suggested that an increase in rotation speed resulted in more removal of oil due to enhanced attrition of soil. The effect of stirring speed increases the abrasion or attrition of soil. As the stirring rate increases, the agitation and abrasion force created in the reactor favours the exposure of the soil surface area to the solutions.

At high stirring speed of 480 and 600 rpm no much differences in oil removal from the non-weathered samples was noted. Therefore, based on economic reasons, 480 rpm was viewed as the optimum condition. For instance, at 360 to 600 rpm, the plots of  $R_n$  and  $SDS_n$  for Soil – 3 showed crude oil removal similar to those of Soil – 1, while Soil – 4 and Soil – 5 showed a constant removal of oil after 480rpm, therefore, stirring speed of 480 is enough to achieve maximum removal of oil.

#### **4.3.4 Effect of washing time**

Time is an important factor in the monitoring process. In any process, factors like cost are always taken into consideration to check its viability and feasibility. The oil removal at different time intervals is presented in Figure 4.44. The choice of 1-minute washing was due to the trend of oil removal in Section 4.2.1.6. However, 1-minute washing is not practically possible to achieve the level of washing expected with the different soils employed in this study. For instance, oil will not desorbed from the weathered soil samples as quick as those of the non-weathered samples.



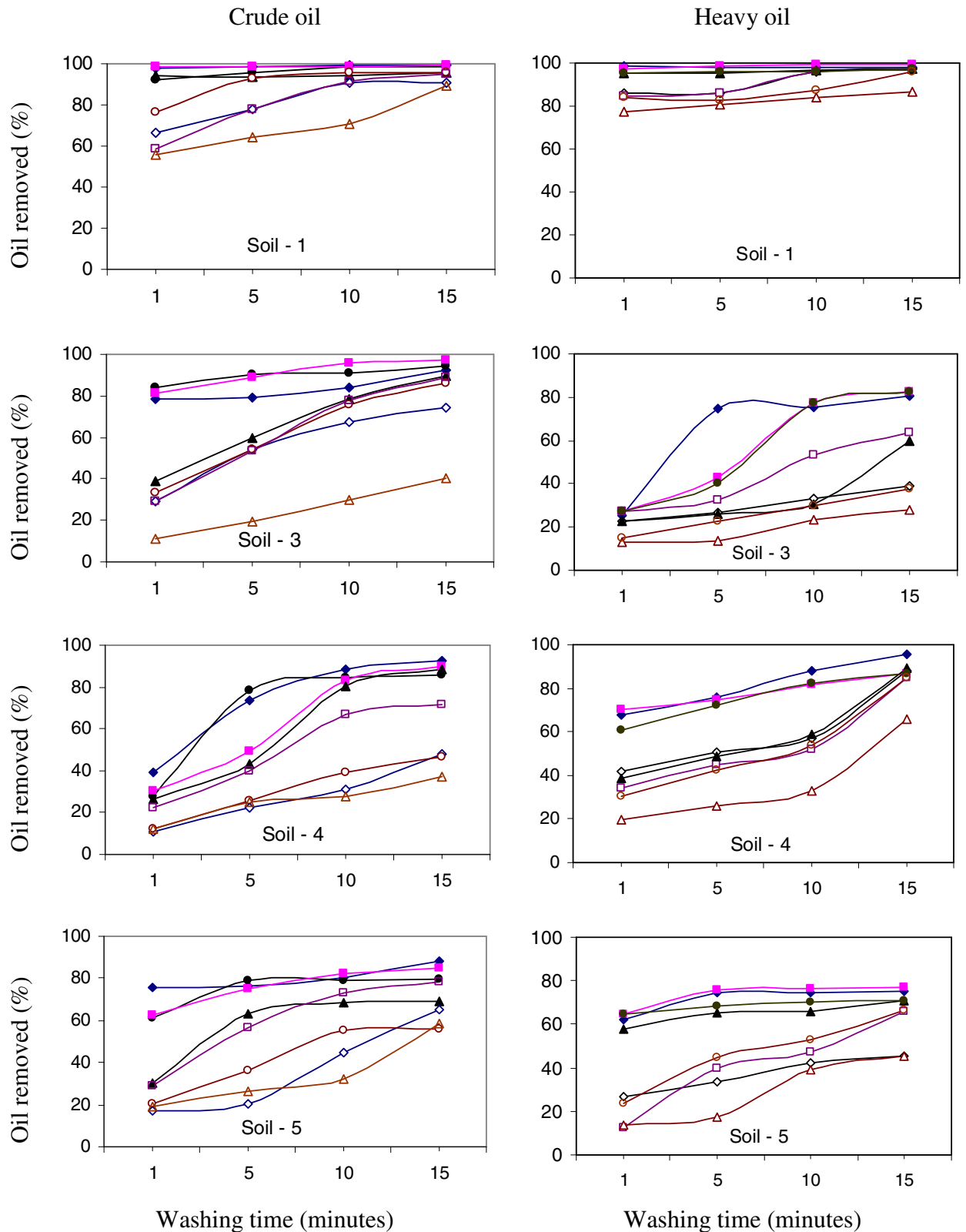


Figure 4.44. Oil removal as function of washing time (washed with 30 cm<sup>3</sup> 0.1%-mass solution at 20<sup>0</sup>C and 480 rpm).

—◆— Rn —●— Sn —■— SDSn —▲— Wn —◇— Rw —○— Sw —□— SDSw —△— Ww

As the washing time increase up 15 minutes, the removal of oil by surfactant solutions from the two contamination cases (weathered and non-weathered soil samples) appears to be the same. Although slight differences were notice during the washing of weathered samples of Soil – 4, this maybe attributed to the varied particle soil sizes. With the diverse particle sizes associate with Soil – 4, rhamnolipid and saponin interfacial interaction with the contaminated soils may be impeded thus they may not act as fast as SDS owing to the fact of their high sorption to soil of 75 and 66.7% respectively. SDS have stable foams, this may be responsible for the better oil removal. This is also applicable to saponin with better foaming ability than rhamnolipid

Since oil has high interfacial tension with water (Section 4.1.2) and low solubilization (Section 4.1.6) in water, the results indicated that the present maximum washing time of 15 minutes will not favour oil removal using distilled water. However, comparing Figure 4.40 and the present study, notwithstanding the amount of contaminated soil of 10g washed and the maximum washing time of 15 minutes, the oil removal using distilled water and surfactants was more enhanced in the stirred tank reactor. Therefore, this present study gives an idea that soil washing in stirred tank reactor will enhance oil removal due to the nature of stirring.

#### **4.3.5 Effect of volume/mass ratio**

Oil removal from 10 g of the contaminated soils was investigated by varying the washing solution volume from 20 to 50 cm<sup>3</sup>. It was expected that as the volume of washing solution increases oil removal would be enhanced. This is because increasing the volume of aqueous surfactant solutions will provide more surfactants micelles or monomers that will act at the interface between the soil and oil. This action will reduce the interfacial tension between the oil and water thereby contributing to the displacement of the oil from the soil by the surfactant. However, the result of oil removal shown in Figure 5.45 does not indicate such trend. For instance, during the washing of the non-weathered soil samples, oil removal either increased or remained constant as volume/mass ratio increased and for the weathered samples, increase in volume did not significantly enhance the oil removal; in some cases there was a reduction in oil removal as volume/mass ratio is increased.

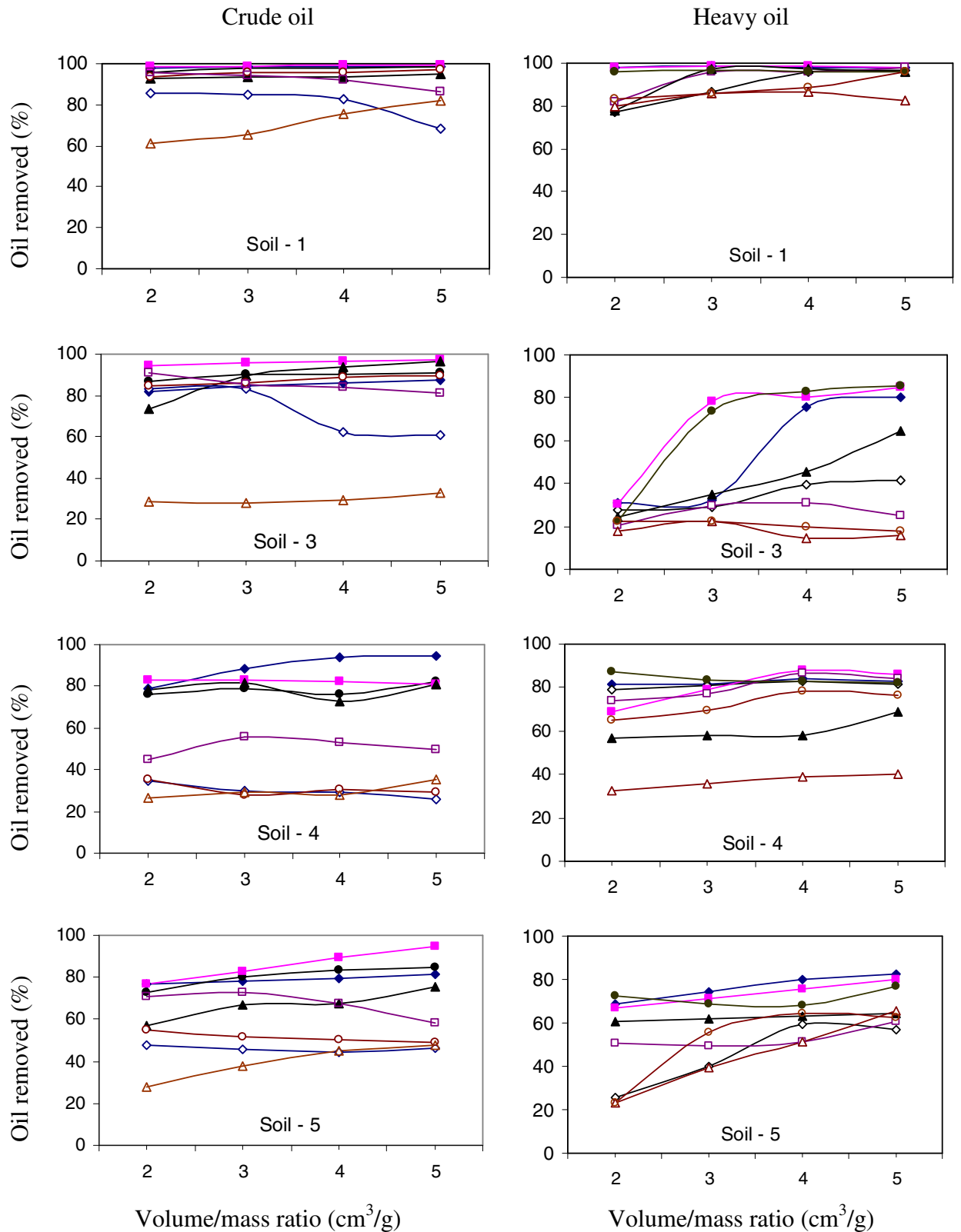


Figure 5.45. Oil removal as function of volume/mass ratio (washed at  $20^\circ\text{C}$  and 480 rpm with 0.1%-mass solution for 10 minutes).

—◆— Rn —●— Sn —■— SDSn —▲— Wn —◇— Rw —○— Sw —□— SDSw —△— Ww

Due to the downward trend in oil removal the experiment was repeated thrice and the results were the same. It was noted that during washing the washed water and oil stick at the wall of the reactor. As the volume of the washing solutions increases, more of the effluents already removed from the soil were noted to stick at the walls. During the analysis of the oil removal from soil with n-hexane, this removed oil was re-introduced into the soil, thereby increasing the oil content in soil. The reduction in oil removal as volume/mass ratio increased was mainly observed for the weathered samples. This behaviour may be due to the concentrated nature of the soil after weathering which lead to contaminated soil with oil of high molecular weight, viscosity and density as noted by Payne and Phillips (1995). This may result in repulsion between the contaminated oil and the surfactant solution, thereby reducing their interfacial interactions. Therefore, the maximum oil removal obtained with 20 cm<sup>3</sup> indicated that such a volume is enough to create the displacement between oil from soil.

The slight increase in oil removal from the non-weathered samples may be due to the formation of emulsions. It was noted in Section 4.1.5 that increasing the concentration of aqueous surfactant solutions and the volume ratio of surfactant solution to crude oil would lead to the formation of emulsions. Invariably in the soil washing study where a constant mass of contaminated soil was washed, increasing the volume of the washing solutions may contribute to the increase in the surfactant concentration. Emulsion formation will aid in the removal of oil from soil, by reducing the interfacial tension between the oil and water: leading to the dispersion of oil into the water phase. Therefore, emulsions aiding oil removal will be favourable for fresh contaminated soils.

#### **4.3.6 Washing with 99% pure rhamnolipid**

The rhamnolipid solution used so far was prepared using a fermentation broth of 15% rhamnolipid. It was not known whether the impurities in the fermentation broth would effect the surfactant action. Therefore, washing study based on pure rhamnolipid (99%) was conducted. The non-weathered crude oil contaminated soil samples of Soil – 4 were investigated in this test. The result of this study is shown in Figure 4.46, it was noticed that between the concentration of 0.004 and 0.2%-mass, the pure rhamnolipid solutions enhances oil removal more than the fermentation broth. However, as the concentration of surfactant solution increases up to 0.1 and 0.5%-mass, the removal of oil was noticed

not to be changing. As the fermentation broth and the pure rhamnolipid have the same CMC of 0.02%-mass, it may be concluded that the pure rhamnolipid would enhance oil below the CMC value. However, depending on the cost of purifying the fermentation broth to 99% rhamnolipid, the fermentation broth may be considered a better option since the removal of oil at 0.1%-mass solution are the same.

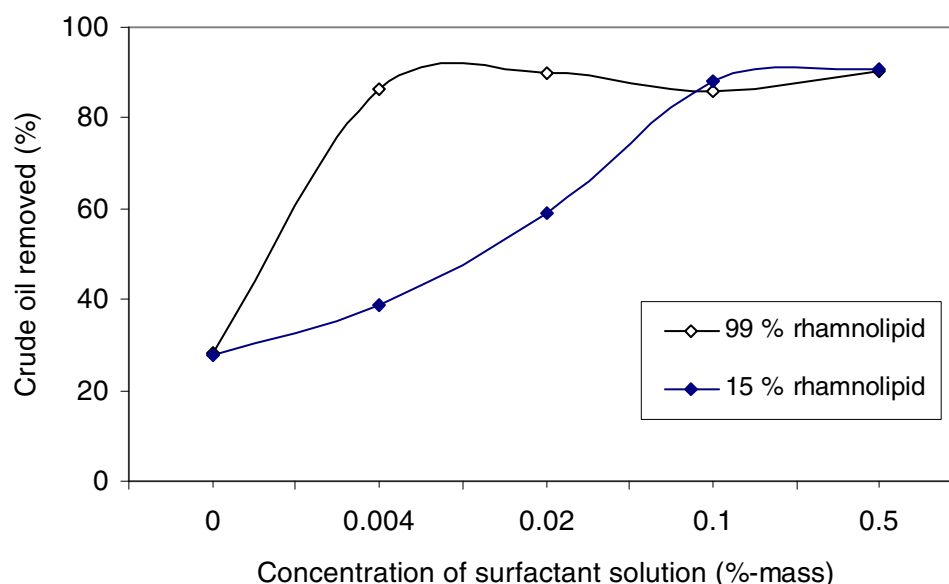


Figure 4.46. Crude oil removal as function of surfactant concentrations (washed at 20°C and 480 rpm with 30cm<sup>3</sup> solution for 10 minutes).

#### 4.3.7 Contaminated soil washed after six months

It should be noted that the contaminated soils are used for soil washing within two weeks of contamination. Therefore, to understand the effect of ageing of the contaminated soil after storing in the glass container for six months, samples of Soil – 4 were washed with rhamnolipid solution. The results of the study showed that crude oil removal with the weathered soil samples was not changing. For the non-weathered samples, reduction in crude oil removal was noted in Figure 4.47. Although this reduction was not significant, it indicated that the non-weathered soil samples have undergone weathering, and would weather more if the sample remains for a longer time. Therefore, surfactant application in oil removal from soil will be more effective in treating non-weathered as well as aged contaminated sites.

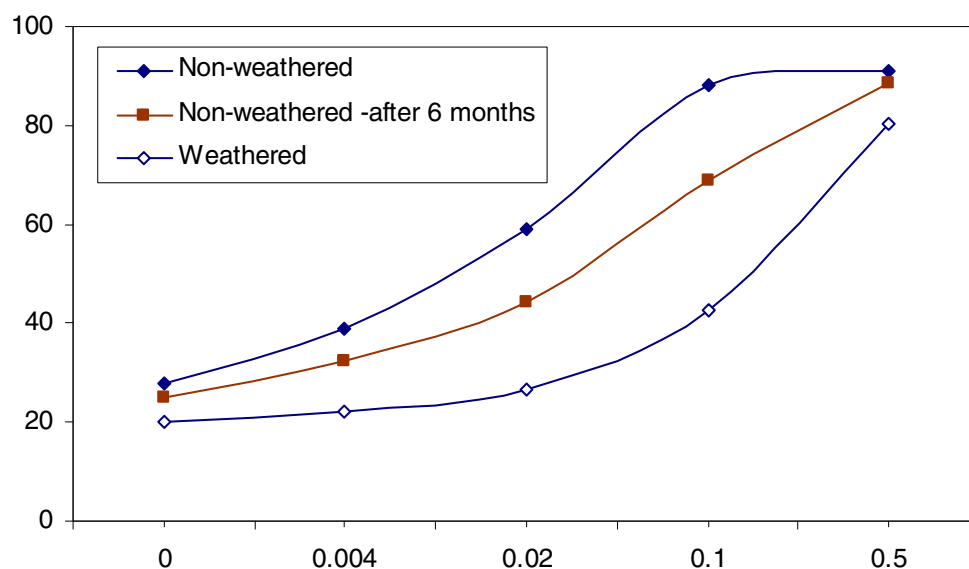


Figure 4.47. Crude oil removal as function of surfactant concentrations (washed contaminated soil after six months at 20°C and 480 rpm with 30cm<sup>3</sup> solution for 10 minutes).

#### 4.3.8 Seawater washing

The removal of oil from the non-weathered samples of Soil – 1 and Soil – 4 was tested with solutions of rhamnolipid, SDS and saponin prepared using seawater as solvent and the effects of solution concentration and washing temperature investigated. The most important reason behind the seawater test was perhaps there is soil contamination within a nearby sea, the ready availability of seawater in the sites will remove the need of providing fresh water. Also the use of seawater will represent a more practical situation, since fresh water may not be available in the site when handling large volume of contaminants.

The two parameters (washing temperature and surfactant solution concentration) investigated were chosen since they directly affect the surface activity of surfactant and the oil. The washing of the non-weathered soil samples of Soil – 1 can simulate washing drill cuttings and drilling mud waste generated in oil drilling operations while Soil – 4 with a varied particle soil distribution gives a general idea of cleaning up a fresh contaminated site.

#### 4.3.8.1 Effect of solution concentration

The effect surfactant concentration in oil removal is shown in Figure 4.48. Contrasting Figure 4.41 and Figure 4.48, the oil removal appears to be the same for Soil – 1. However, during the washing of Soil – 4, at zero concentration, there was enhancement in crude oil and heavy oil removal of about 40 and 70% respectively. Since it have been noted in Section 2.6 that the addition of electrolyte such as sodium ions will reduce the electrostatic repulsion between the similar ionic heads of aqueous solution of surfactants, it is not surprising to have similar oil removal using either distilled water or seawater from Soil – 1. This could be explained by understanding that Soil – 1 had a large surface area, which is associated with large electric charges; this negative charge will counteract those ions contributed by the electrolyte thereby resulting to washing solution that similar to distilled water.

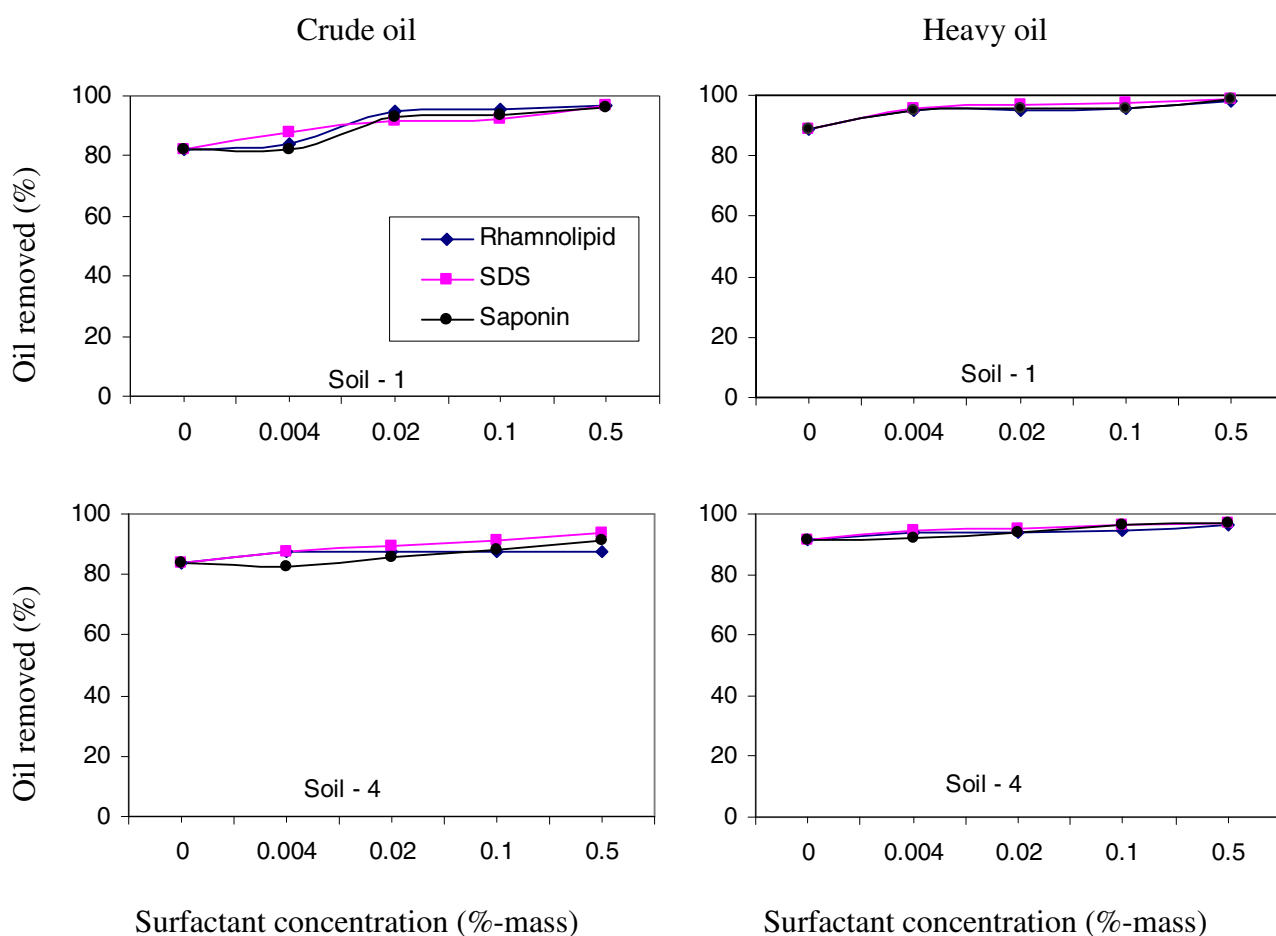


Figure 4.48. Oil removal versus concentration surfactants. Washed at 20<sup>0</sup>C with 30cm<sup>3</sup> solution at 480 rpm for 10 minutes.

In Soil – 4, the enhancement in oil removal using seawater appears to be dependent on the effect of electrolyte. The addition of electrolytes will lower the surfactants CMC and probably increase the aggregation number and micelle size. Although it has already been noted in Section 4.2.1.2 that oil removal is not due to solubilization of the oil in the micelle interior, however, the reduction in CMC of the surfactant solutions in the presence of electrolyte may contribute to the ultra low interfacial tension in oil-water systems. Therefore, the applicability of the study will be appreciated in treatment of surface contaminated soils (Soil - 4) and waste soils (Soil – 1) generated through drilling operations.

#### ***4.3.8.2 Effect of washing temperature***

The effect of temperature shown in Figure 4.49 indicates oil removal using the seawater prepared solutions is similar to those of distilled water (Figure 4.49). The similarity appears to be due to the inverse relationship of oil viscosity and temperature (Section 4.2.1.1). However, slight differences are noted from Soil – 4 between 5<sup>0</sup>C and 20<sup>0</sup>C, where the seawater solutions performances are better. Although the surfactant sorption to soil in Section 4.1.4 indicated that the surfactants lost in seawater were more than in the distilled water, the better removal could be explained due to the effect of electrolyte lowering the CMC, which was given in Section 4.3.8.1. Generally, the use of seawater as a washing solution in ex-situ soil washing technology seems to be a better option than using fresh. This implies that the treatment of contaminated soil may be carried out near a seawater source thereby making the process time and cost effective.



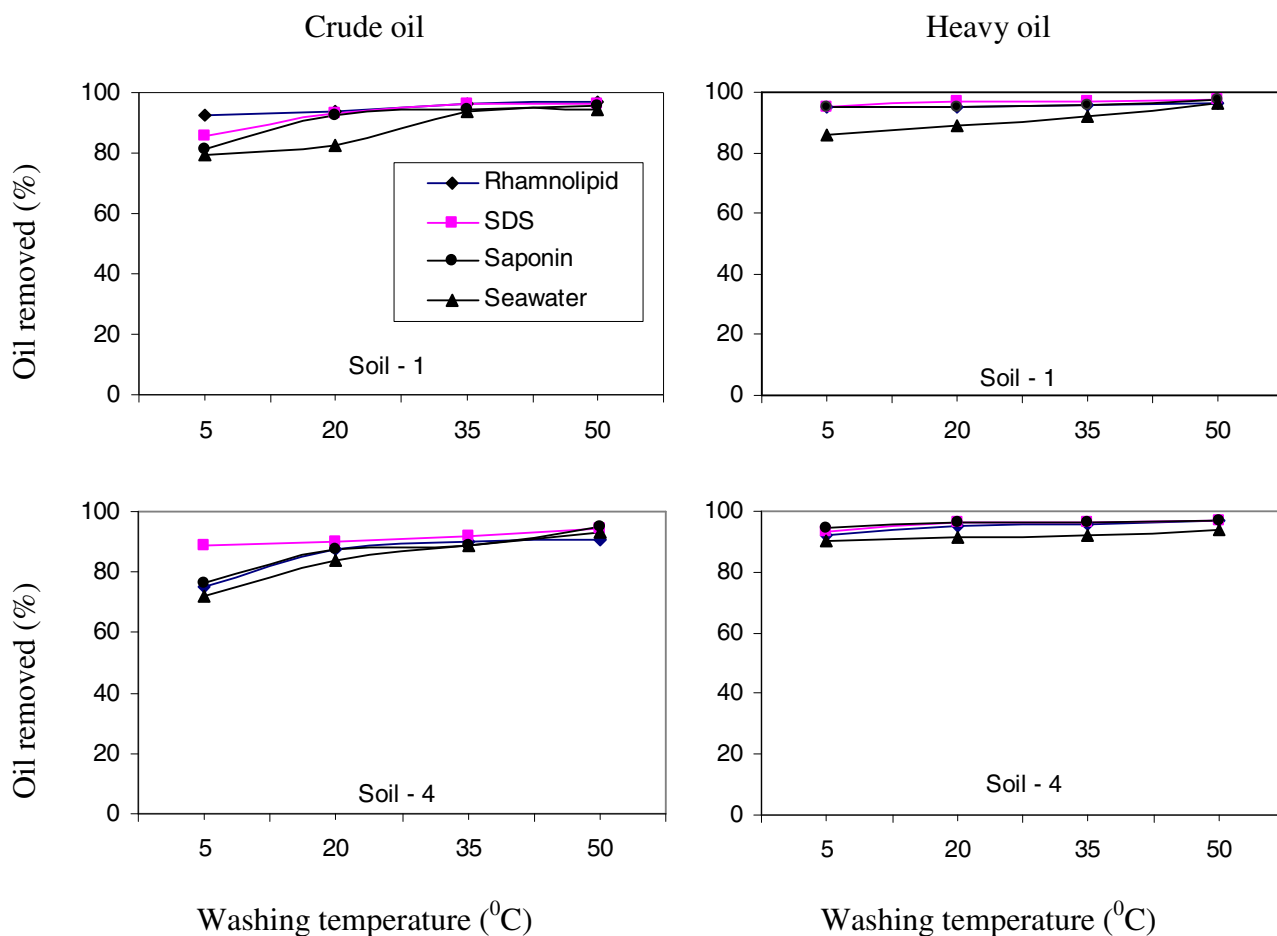


Figure 4.49. Oil removal versus temperature. Washed with 30cm<sup>3</sup> 0.1%-mass solutions at 480 rpm for 10 minutes.

#### 4.3.9 Conclusions

Soil washing in stirred tank reactor was examined to mimic the ex situ technique. This study employed two contaminants (crude oil and heavy oil) and the amount of contaminated soil washed was scale up to 10g. With emphasis on crude oil, the oil removal from the different soil fractions (Soil – 1, Soil – 3, Soil – 4 and Soil – 5) were used to simulate the effect of the range of soil particle fractions found naturally.

- Critical examination of the results indicated that the performance of the surfactant solutions in removing oil was relatively dependent on their physiochemical characteristics, foaming abilities, soil particle size distribution and nature of oil.
- All the surfactant solutions showed approximated constant oil removal of more than 95 and 90 % from the non-weathered and weathered samples of Soil – 1. The greater oil removal was attributed to the interaction of surfactant/soil (such as sorption of

surfactant to soil) and surfactant/oil (such as interfacial tension reduction, solubilization and emulsifications), which dominate the interaction of oil/soil.

- The disparity in crude oil and heavy oil removal from Soil – 1, Soil – 3, Soil – 4 and Soil – 5 was due to the resulting complex nature of crude oil after weathering. The disparities were more pronounced as the soil particle fraction is increasing. The low oil removal from larger fractions of the weathered soil samples was due to the surface roughness of the soil. As the soil samples have grooves and cavities, the oil will stick inside the soil pores and reduce the surface interaction with the surfactants.
- Surfactant with low molecular weight, and less bulk and complex hydrocarbons chains was observed to have greater oil removal. Saponin has the largest weight and more complex followed by rhamnolipid and then SDS, oil removal from Soil – 3, Soil – 4 and Soil – 5 was in the following descending order: SDS<sub>n</sub>, S<sub>n</sub> and/or R<sub>n</sub> and SDS<sub>w</sub>, S<sub>w</sub> and R<sub>w</sub>. The order of oil removal appears to be the same as order of surfactant foaming stability and sorption to soil.
- Washing solutions showed a considerable oil removal as the temperature is increased.
- The slight increase in oil removal from the non-weathered samples during the effect of volume/mass ratio may be due to the formation of emulsions. Increasing the concentration of aqueous surfactant solutions and volume ratio of surfactant solution to crude oil would lead to the formation of emulsions. Emulsions aiding oil removal will be favourable for fresh contaminated soils. However, the maximum oil removal obtained with 20 cm<sup>3</sup> solutions suggested that such a volume is enough to create the displacement of oil from the weathered soil samples.
- The pure rhamnolipid solution removed oil below the CMC. Depending on the cost of purifying the fermentation broth to 99%, the rhamnolipid with 15% purity may be considered a better option since their oil removal at 0.1%-mass was the same.
- Crude oil removed from the weathered samples was not changing after storing in the glass container for six months. For the non-weathered samples, the reduction in crude oil removal suggested the effect of weathering. The weathering may persist if the soil sample is kept for longer time.
- The used of seawater represent a real life situation, since fresh water may not be available in the site when handling large volume of contaminants.
- With Soil – 4, the enhancement of crude oil and heavy was more than 40% and 70% respectively. The electrolyte in seawater reduces the electrostatic repulsion between

the similar ionic heads of aqueous solution of surfactants. For Soil – 1, it is not surprising to have similar oil removal using either distilled water or seawater. This could be explained by the fact that Soil – 1 has a large surface area, which is associated with large electric charges; this negative charge will counteract those ions contributed by the electrolyte thereby resulting to a washing solution that is similar to distilled water.

- The applicability of this study would not only be on the treatment of soils contaminated by petroleum oil spills, but on managing contaminated soils generated through drilling operations that are improperly disposed.

## **4.4 Soil washing in air sparging assisted stirred tank reactor**

In order to find an effective and reliable method for removing oil from contaminated soils through the ex situ technique, the floatation method was tested with the aid of two surfactants. Oil removal was conducted with 200 g of Soil – 4 samples. Soil – 4 was used for this study because it is composed of particle fractions that are mainly encountered in nature. Also, due to the low percentage of fine fractions (3%) in Soil – 4 (Section 3.1.1.2), the possibility of formation of undesirable emulsions was avoided as noted in Varadaraj (1995).

The flotation technique is based on the ability of the oil to attach to the air bubbles (foams) for effective removal from the contaminated soil. The two surfactants (rhamnolipid and sodium dodecyl sulfate) used were prepared in distilled water or seawater. Generally, Rosen (1989) have recommended the anionic surfactants for flotation experiments because of their low sorption to soil in comparison to non-ionic ones and their better foam stability. For the purpose of this study, they are used because of the availability and it was considered that their performances in the previous studies were good.

### **4.4.1 Effect of air sparging**

To understand the effect of air sparging (compressed air) and stirring at 480rpm, 200g of the contaminated soil was washed with 350 cm<sup>3</sup> 0.1%-mass solution of rhamnolipid at 20<sup>0</sup>C for 20 minutes. The results showed that crude oil removed was about 92.31%. When the washing was conducted with stirring only (no air) the crude oil removed reduced to 80.49%. Therefore, air sparging attributed about 12% increment in crude oil removal. The effect of air sparging increases the foaming of the surfactant solutions thereby increasing the contact between contaminated soil and surfactant. Since oil is hydrophobic in nature, it is strongly attracted to the foams, which readily displaces water at the solid surface. Hence, the separation of oil from the contaminated soil may be accomplished by the selective attachment of the oil to air bubbles (foams) and the hydrophilic particle remaining in the water phase. In addition, due to the good permeability of the Soil – 4 (Section 3.1.1.6), the flow of surfactant solutions and air bubbles in the reactor was steady and easy in percolating through the soil mass.

The effects of the different parameters studied in oil removal from the soil are presented in the subsequent sections.

#### **4.4.2 Effect of temperature**

In order to find out the oil removal effectiveness of the surfactant solutions, a flotation experiment was conducted at different washing temperatures. The results of these tests as a function of temperature are shown in Figure 4.50. As can be seen, the results of this study showed that temperature increase does not enhance crude oil removal from the non-weathered soil samples. The weathered samples indicated that as temperature increased, crude oil removal is enhanced, except for SDS which showed an almost constant crude oil removal of about 85%. The similarity in oil removal between rhamnolipid and SDS may be due to the constant foam that was produced during the washing. For the heavy oil, above 20°C, rhamnolipid and SDS showed more than 85 % oil removal, which is greater than the removal obtained from the weathered soil samples with any of the washing solutions at 50°C. The lower removal at 5°C indicated that weathered oil exhibits an adhesive behaviour with soil and as a result, remains attached to the soil particles once they are entrapped.

With respect to all the parameters tested, only temperature shows a direct correlation with the physical properties of oil, such as viscosity and density. As the oil temperature increases, viscosity reduces; this invariably will enhance the removal of oil from soil. The overall study indicated that both crude and heavy oil removal from soil show a similarity in their trend. However, crude oil removal was more enhanced than heavy oil. Considering the range of temperatures tested and the viscosities of the oils in Section 3.1.2, it can be deduced that oil viscosity plays a significant role in oil removal from soil. Further, reduction in viscosity will lead to the mobilization of oil, which creates an avenue for the separation of oil from soil.

Also, the slight higher heavy oil removal against crude oil as seen in some of the figures for the weathered samples indicates the resulting complex nature of crude oil during weathering. As the chemical compositions (trace metals, organic and inorganic materials) of crude oil concentrates during weathering, the oil binds more to the soil; this might render the surfactant solutions less effective.

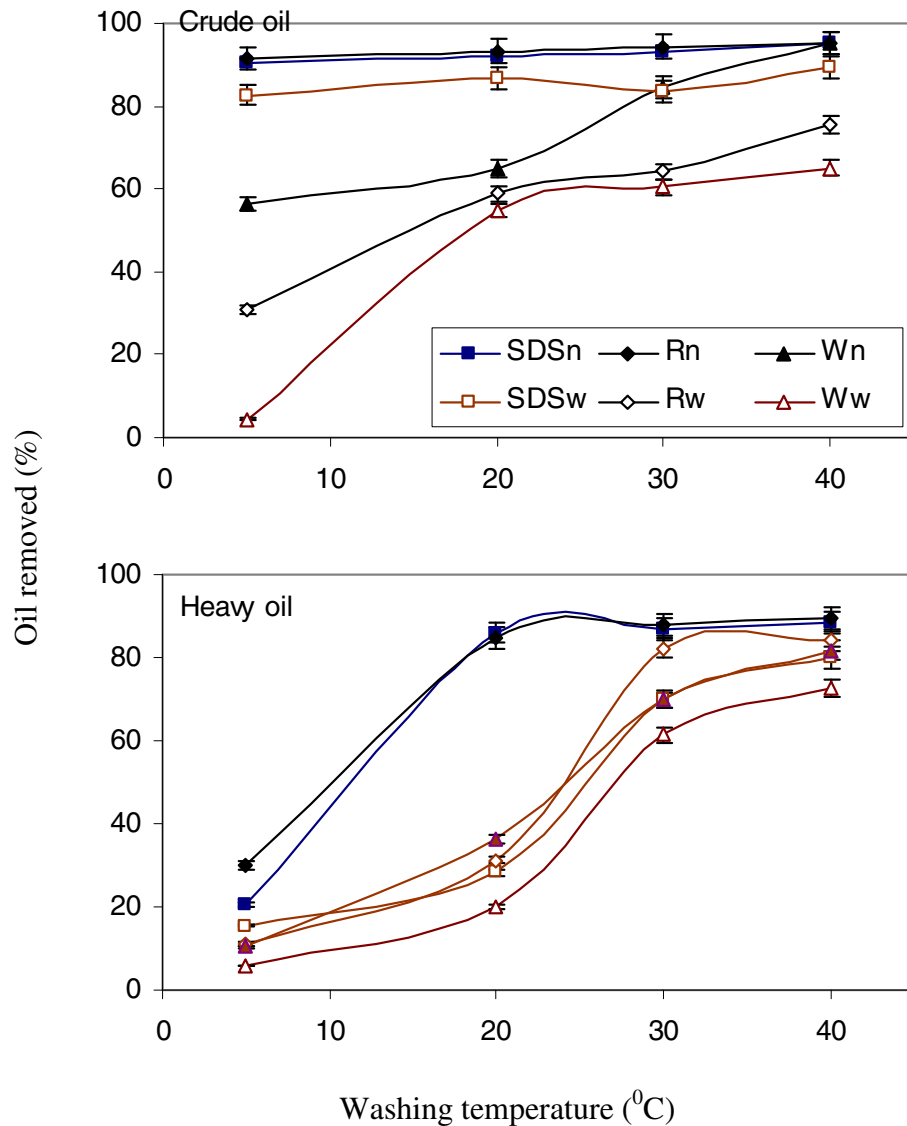


Figure 4.50. Oil removal as function of washing temperature (washed with 350 cm<sup>3</sup> 0.1%-mass solution washed for 10 minutes).

#### 4.4.3 Effect of surfactant concentrations

Flotation washing was conducted to investigate oil removal from soil by increasing the concentration of surfactant solutions from zero (distilled water, W) to 0.5%. This range of solution concentrations is believed to be useful in effective oil removal from a real life contamination. The results of these studies shown in Figure 4.51 indicated that crude oil removal from the non-weathered samples is enhanced between zero and 0.02 %-mass and then remains constant. It is of interest to mention that there was no formation of emulsions during washing even when the solution concentration was

increased up to 0.5 %-mass against 0.1 %-mass recommended by Somasundaran et al. (1997) and Clifford (1993).

As there is no emulsion formation, three things were deduced: it is believed that the soil sample does not have silt and clay fractions that may contribute to formations of stable emulsions as noted by Varadaraj (1995). Also, due to the effect of foam generation, the oil is removed from the soil by surfactant, but instead of the oil remaining in the bulk surfactant phase forming a liquid-liquid dispersion, the oil is carried away by the foams thereby forming a gas-liquid phase. This will eventually reduce the amount of oil that may disperse in the bulk surfactant phase to form emulsions.

During the washing of the weathered soil samples, the disparity in crude oil removal between SDS and rhamnolipid may be due to the differences in their physicochemical properties such as sorption to soil and foaming. Contrasting SDS with rhamnolipid, the oil is concentrated with higher molecular weight hydrocarbons thereby, making the contaminated soil more hydrophobic. Since surfactant solution is used to reduce the hydrophobicity of the oil phase by lowering the interfacial tension and detach itself from the soil surfaces, the surfactant sorption to soil (Section 4.1.4), and their foaming abilities (Section 4.1.3), will contribute to their oil removal efficiencies. With the generation of foams where the oil will adhere to, there is greater possibility for SDS to carry out more oil due to its greater foaming production and less sorption to soil.

For the heavy oil, results showed that oil removal from the non-weathered samples were similar to those of crude oil while the weathered soil samples oil removal increased beyond the CMC. The lower removal of heavy oil from the weathered soil samples was due to the weathering of the contaminated soil, which led to the stronger attachment of the contaminated soil thereby making them difficult to be washed. At 0.5%-mass heavy oil removal by the two-surfactant solutions was similar to that of rhamnolipid in removing crude oil. Therefore, oil removal from the non-weathered soil samples would be effective at low solutions concentrations (such as 0.02%-mass). Flotation beyond this concentration would not offer any advantage.

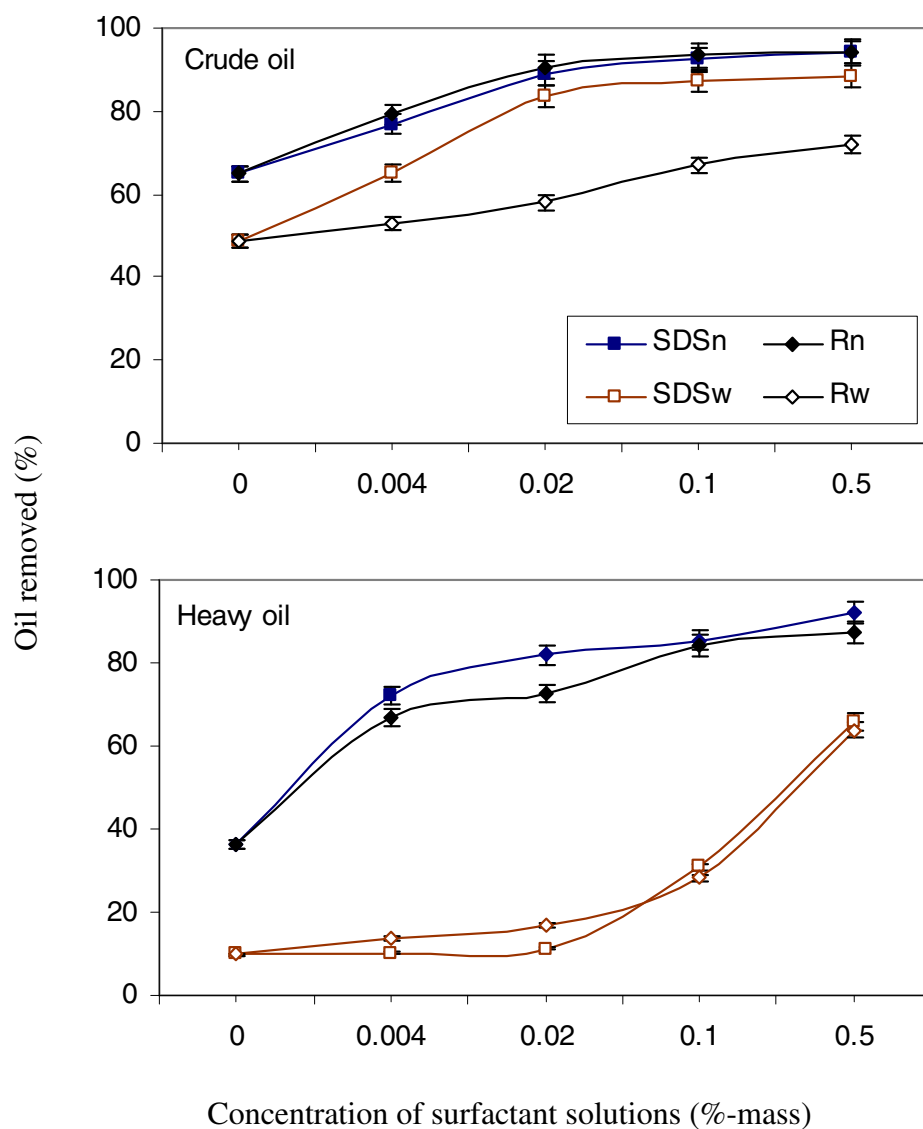


Figure 4.51. Oil removal as function of concentration surfactant solutions (washed at 20<sup>0</sup>C with 350 cm<sup>3</sup> solution for 10 minutes).

#### 4.4.4 Effect of volume/mass ratio

Experiments were performed to determine the amount of oil removed from 200g of contaminated soils by varying the volume of washing solutions. Results obtained from these studies are presented in Figure 4.52. It can be seen that the heavy oil removal is less than that of the crude oil from both weathered and non-weathered samples. Constant crude oil removal was observed over the range of volume of solution tested for the non-weathered samples and the divergence between rhamnolipid and SDS was negligible. This indicated that the volume of surfactant solution (150 cm<sup>3</sup>) was enough



to create a high density of sparged air in the reactor. In addition, Zhang et al. (2001) have noted the effect of the volume/mass ratio during the flotation of 30 g of artificially contaminated soil sample with 120 and 200 cm<sup>3</sup> solutions of SDS and found out that there are little differences between the two test results. This may be due to the fresh nature of the contamination, which is similar to the non-weathered crude oil contamination soil samples.

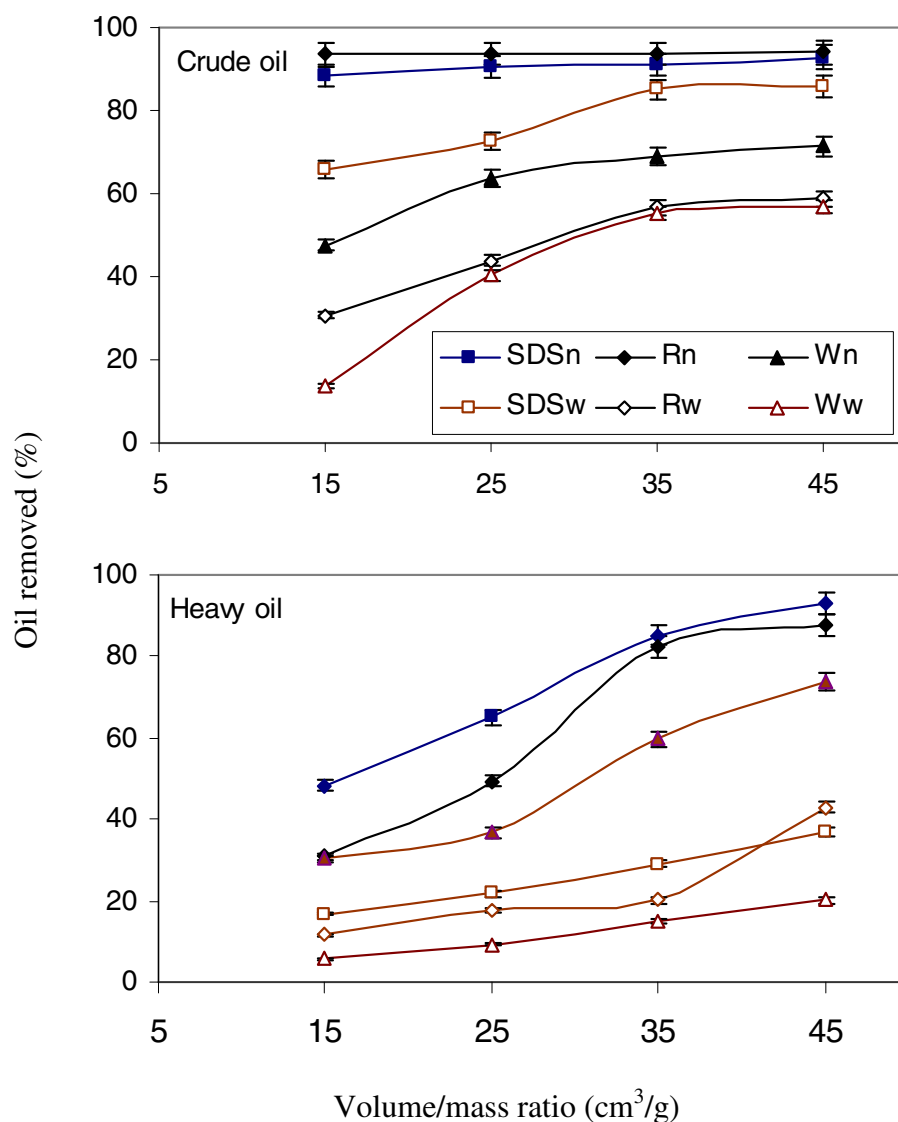


Figure 4.52. Oil removal as function of volume/mass ratio (washed at 20°C with 0.1 %-mass solution washed for 10 minutes).

However, for the crude oil weathered samples and the weathered and non-weathered samples of the heavy oil, it can be seen that the removal of oil increases as volume of solution is increased as result of more surfactant micelles or monomers being available to interact with the oil at the interface. All the washing solutions showed a steep

increase in oil removal between the volume/mass ratios 15 and 35 from the weathered sample and then remain constant. This gives an idea that the removal of crude oil from the weathered soil samples would be effective with 350 cm<sup>3</sup> solutions whereas the removal of heavy oil indicated that more oil removal would have been possible if volume were to be increased beyond 450 cm<sup>3</sup> with a constant mass of contaminated soil of 200g.

#### **4.4.5 Effect of washing time**

Oil removal was investigated at different time intervals between 5 to 30 minutes. As expected, as time increased from 5 to 30 minutes both the crude oil and heavy oil removal increases as shown in Figure 4.53. The increased oil removal may be attributed to the greater contact time of the surfactants with the contaminated soil. This washing time is thought to be analogous to the wetting of contaminated soil with washing solutions. As the contaminated soil is wetted, the contact angle between the soil and oil would be expected to increase. The increase in the contact angle would be rapid as the washing time is increased which will depend on the oil and contamination nature.

For the crude oil non-weathered samples, exceptions were made from rhamnolipid and SDS. They showed that maximum crude oil removal could be attained within 5 minutes of washing. This constant oil removal maybe attributed to the fresh contamination nature. Therefore, increasing the time of washing beyond 30 minutes may not be practical or economically feasible.

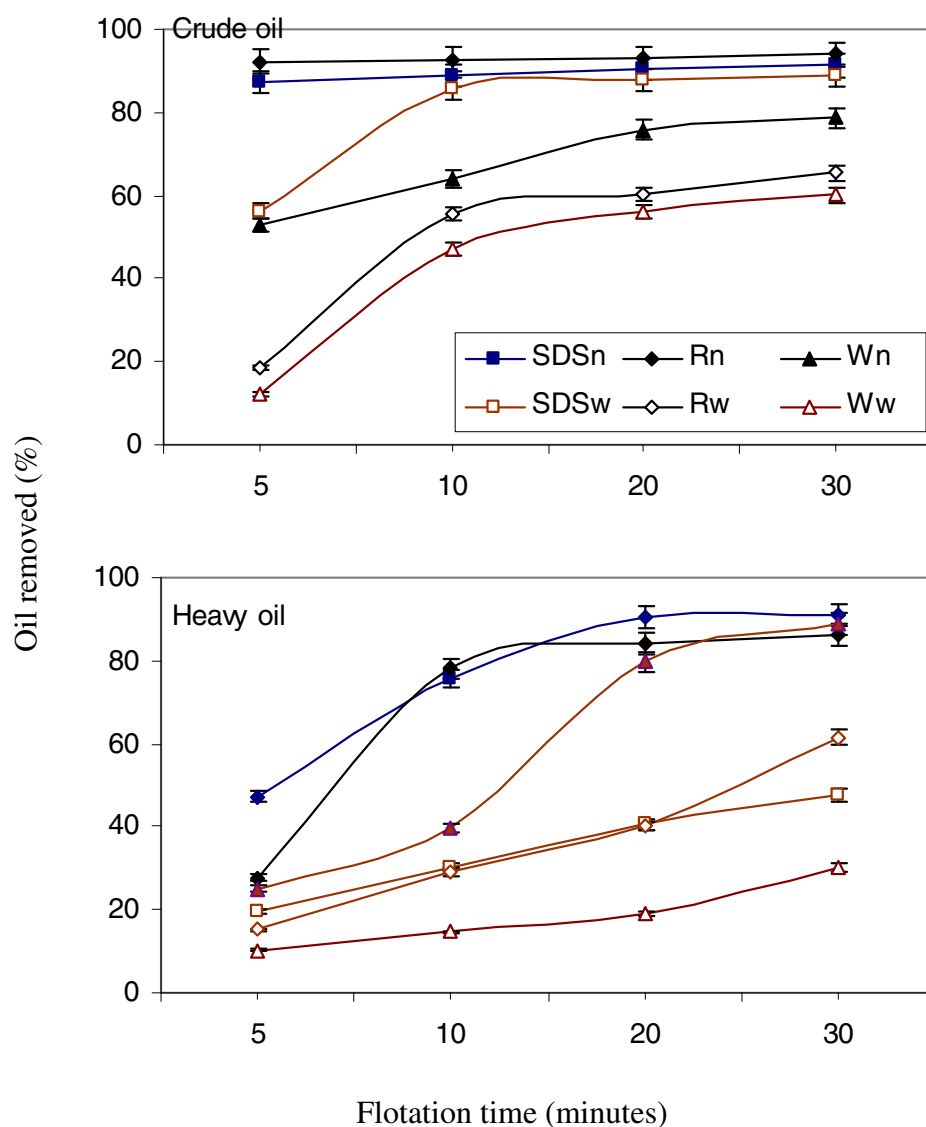


Figure 4.53. Oil removal as function of washing time (washed at 20°C with 350 cm<sup>3</sup> 0.1 %-mass solution).

#### 4.4.6 Seawater washing

These studies showed that seawater and seawater prepared solutions were more effective than those of distilled water prepared solutions. For instance, in Figure 4.54, crude oil removal as temperature increases from 5 to 50°C was greater than 80% at all levels of parameters tested. Although heavy oil at 5°C was approximately the same for distilled water, at 20°C heavy oil removal was more than 30% for some surfactants that were prepared with seawater. Also, the effect of solution concentration study showed similar results as during the effects of temperature as presented in Figure 4.55. The

crude oil removal between rhamnolipid and SDS were the same throughout the study. Heavy oil removal was about 10 to 25% greater for non-weathered and weathered samples in comparisons with distilled water prepared solutions.

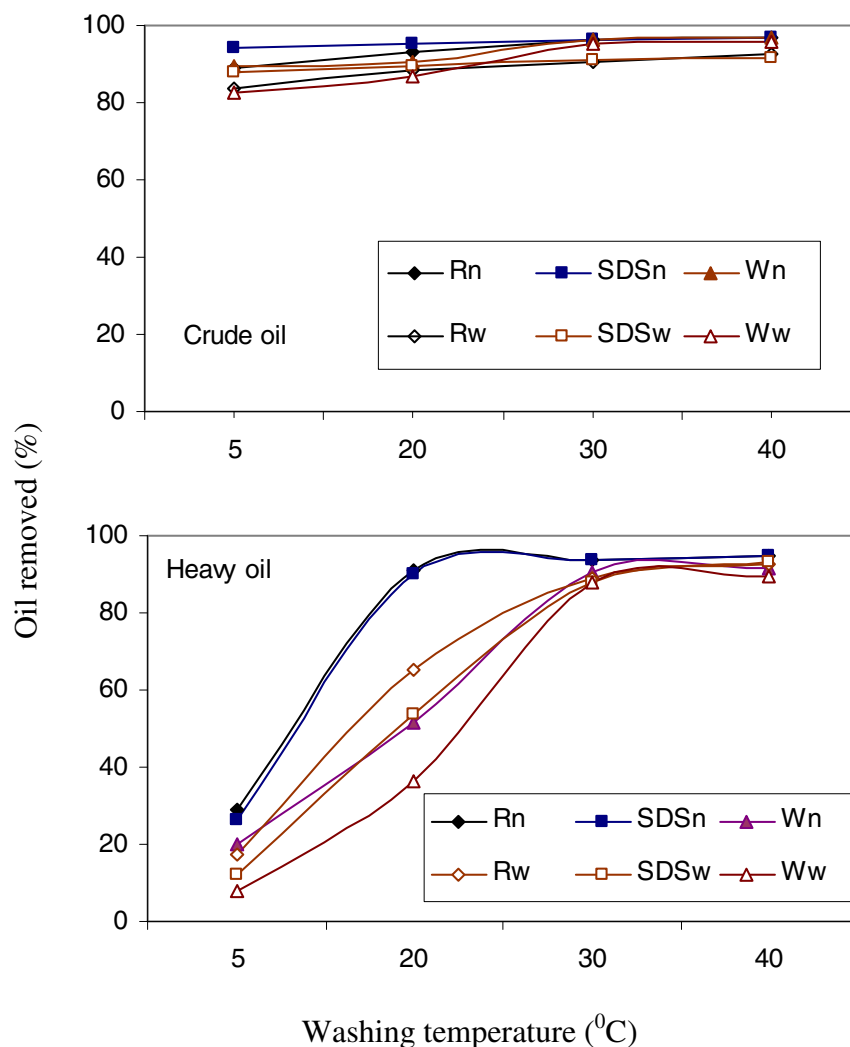


Figure 4.54. Oil removed as function of washing temperature (washed with 350 cm<sup>3</sup> 0.1 %-mass seawater prepared solution for 10 minutes).

The greater removal with seawater may be due to the addition of the electrolyte in the seawater which reduces the electrostatic repulsion of the surfactants (Section 2.6). The effects of the addition of electrolyte on oil removal from soil have been discussed in Section 4.4.6.

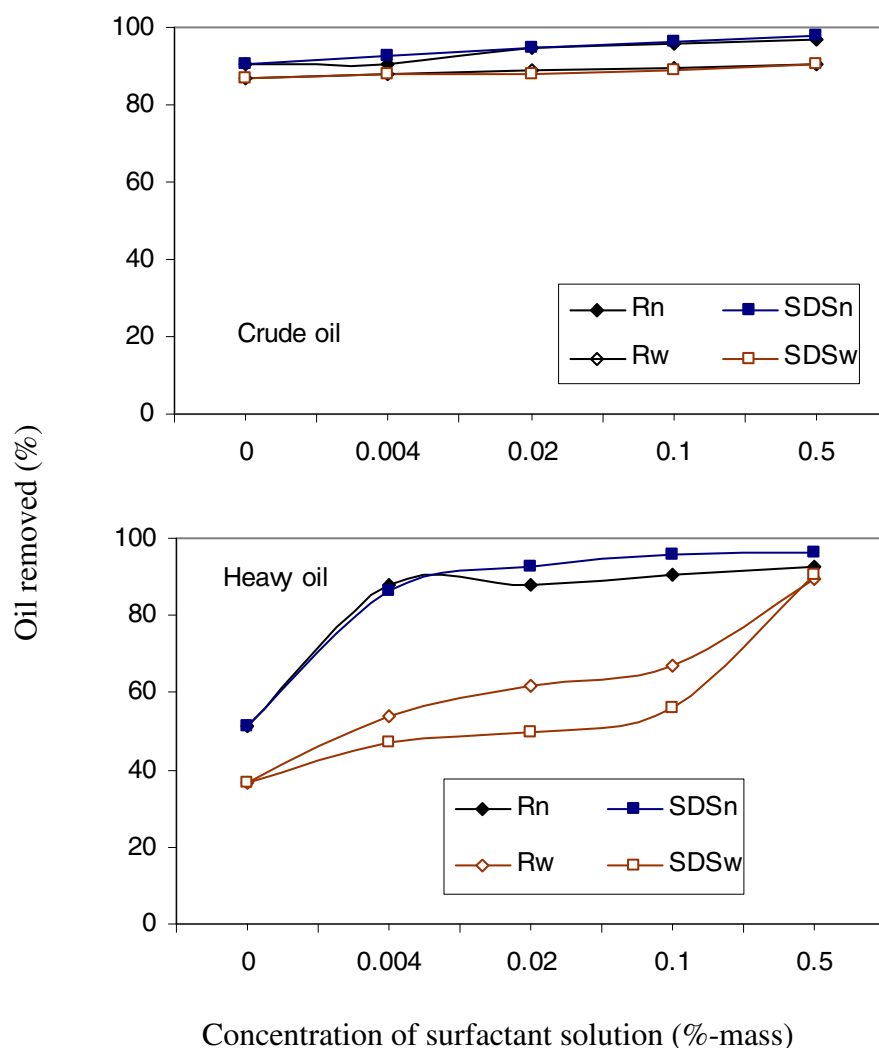


Figure 4.55. Oil removed as function of concentration of surfactant prepared with seawater at 20<sup>0</sup>C with 350 cm<sup>3</sup> solution for 10 minutes.

#### 4.4.7 Conclusions

The removal of petroleum hydrocarbon oil from laboratory-contaminated soil has been studied using surfactant solutions in an air sparging assisted stirred tank reactor. Results showed that oil removal from the non-weathered soil samples could be achieved at first and second parameter levels.

- Oil removal at the different points within the reactor was approximately the same, which indicated uniform mixing.
- Rhamnolipid with loss of about 57% to soil and less foam stability showed an oil removal that was comparable to that of SDS. Sodium dodecyl sulfate showed removal of oil greater than 80% whilst rhamnolipid showed similar oil removal at the third and fourth parameter levels tested.

- The removal of crude oil from the non-weathered soil samples was more effective than that of the heavy oil. The oil removal was not only dependent on the physicochemical characteristics of the washing media but was relatively dependent on the floating of the contaminated soil.
- The heavy oil removal was more significant with seawater prepared solutions, which showed more than 40% in comparison with the distilled water prepared solutions at the first and second parameter levels tested.
- This approach to soil washing was observed to be most effective, therefore was suggested for a field test to assess the efficiency of these surfactant solutions and water.

## **4.5 Column washing**

Soil washing study was conducted in a glass column to simulate the in situ soil washing method. The removal of crude oil and heavy oil was investigated using solutions of rhamnolipid, saponin and sodium dodecyl sulfate that were prepared in either distilled water or seawater. The low solution concentrations tested were in accordance with the work of Bai et al. (1997), and SDS was chosen because there interactions with NAPLs in soil columns are well studied by Liu and Roy (1995), Liu (1997) and Liu et al. (1995). The effect of temperature, pore volume, flow rate and concentrations of surfactant solutions were used to assess the performances of the surfactant solutions.

As limited literature exists on the enhanced removal of crude oil from soil through in situ washing with biosurfactant solutions, ideas gained from literatures such as Liu and Roy (1995), Liu (1997), Liu et al. (1995), Kommalapati et al. (1997), Kommalapati et al. (1998), Roy et al. (1995), Roy et al. (1994) and Bai et al. (1998) on the removal of NAPLs from ground water, aquifers, and sub-surfaces soil will be applied in this study.

The graphs shown in the subsequent sections of this thesis demonstrate the average of oil removed at the bottom, middle and top of the soil column as there was not much difference in oil removal along the soil column, it was less than 3% between each layer.

### **4.5.1 Effect of surfactant concentration**

Experiments were conducted in up flow direction and the results presented in Figure 4.56. As can be seen from the figure, the enhancement of oil removal was first observed between the concentration of zero (distilled water only) and 0.004%-mass. Crude oil removal from the non-weathered and the weathered soil samples with distilled water was about 40 and 20% respectively. This removal was observed to be twice the amount removed during the washing of the heavy oil contaminated soil. As surfactant solution concentration increased from 0.004 to 0.5%-mass, it was observed that oil removal from the soil samples improved. The addition of surfactants is expected to enhance oil removal in two ways: solubilization or mobilization (Section 2.5).

Since the surfactants' solubilization effectiveness is dependent on the ability of the surfactant to increase the aqueous-phase solubility of oil into the hydrophobic core of surfactant micelles, the studies in Section 4.2.1.2 suggested that solubilization is not responsible for the oil removal since high surfactant concentrations are generally required for effective solubilization of oil. With the low surfactant concentrations tested, the effects of both emulsification and solubilization mechanisms were negligible. Therefore, it was thought that mobilization due to the reduction of interfacial tension of oil/water system, which is responsible for the displacement of oil droplets from soil, is behind the removal of oil.

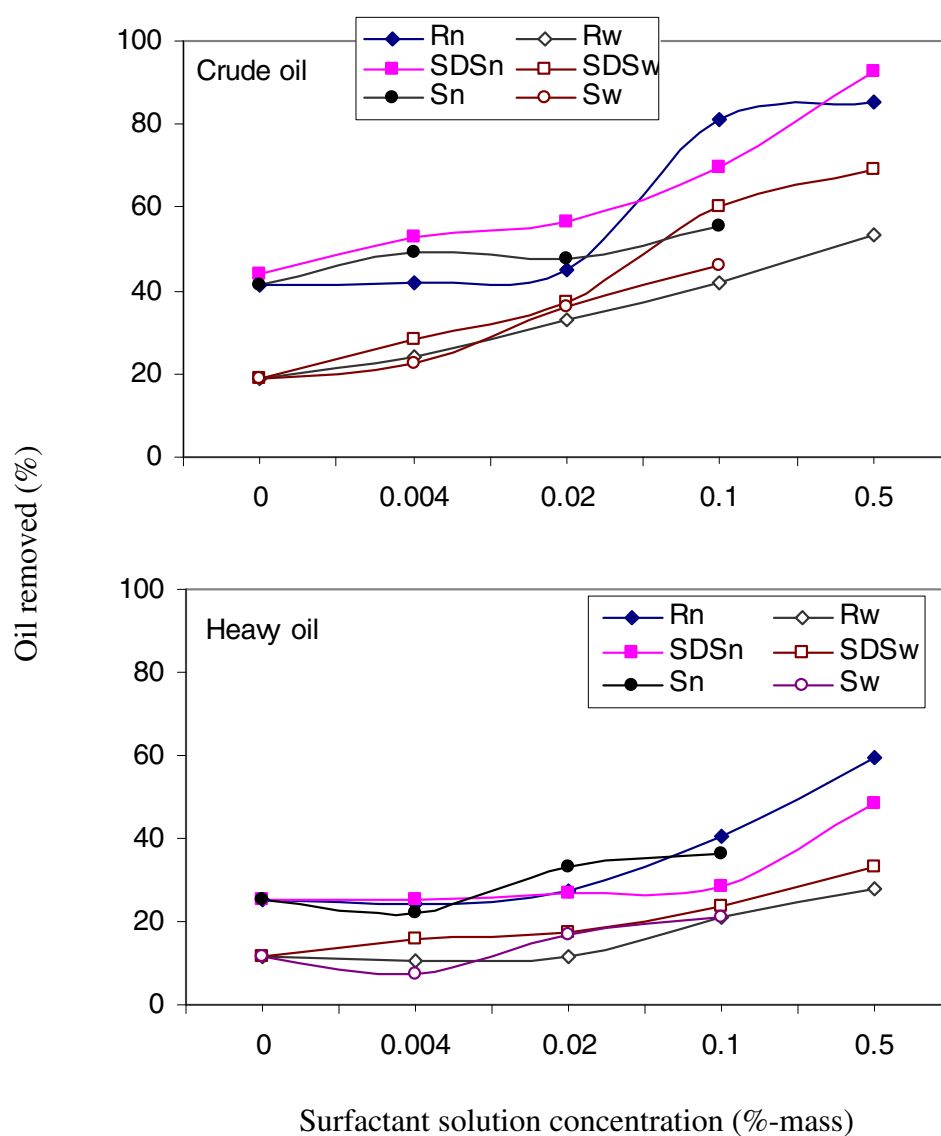


Figure 4.56. Oil removal as function of surfactant solutions concentration: 30 pore volume (PV) pumped at 2cm<sup>3</sup>/minutes at 20<sup>0</sup>C.



Surfactants mobilize oil by lowering the interfacial tension sufficiently for the capillary forces holding the oil in place to be overwhelmed by gravity and viscous forces. Capillary forces are inversely proportional to the soil permeability; the higher the soil permeability or the larger the pore size, the lower the capillary forces and the more easily mobilization will occur. The lower the soil permeability, the lower the interfacial tension value necessary to induce mobilization. The reduction in interfacial tension improves the displacement and dispersion of oil droplets, resulting in higher removal of oil from soil. The surfactant solutions have a negative charge, as do the soil particles. When oil droplets with surfactant molecules around them approach the soil particle, the repulsive forces keep the droplets in suspension and thus are mobilized.

With 0.1%-mass solutions, rhamnolipid and saponin showed about 80 and 60% crude oil removal from the non-weathered samples. At this concentration of 0.1%-mass solutions which is about 5 folds greater than rhamnolipid CMC, rhamnolipid showed a greater oil removal than the other surfactants. SDS indicated that more oil could be removed after 0.5%-mass solutions. The maximum concentration of 0.1%-mass solution of saponin studied was due to its low oil removal after 0.02%-mass as noted in Section 4.2.1.2. Therefore, this study was limited with saponin solution concentration of 0.1 %-mass.

As mentioned in Section 4.3.1, the surfactants' chemical structure and molecular weight plays an important role in their surface activities, therefore, can influence their performances in washing contaminated soils. The surfactant molecular weights and structures in terms of branches are in the following increasing order: SDS, Rhamnolipid, and saponin. Hence, crude oil removal in the soil column was in the following increasing order: saponin, rhamnolipid, and SDS. Rhamnolipid was observed to be more effective than saponin. Therefore, rhamnolipid was selected for detailed study although it shows greater sorption to soil, its performance in oil removal was tested against that of SDS with other parameters.

#### **4.5.2 Effect of flow-rate**

The retention time of solutions in the soil column is directly proportional to their flow rate. As flow rate is increased, the retention time of surfactant solution in the column is

reduced. The oil removal at different flow rate is presented in Figure 4.57. Since the soil has high permeability the flow of surfactant solutions was not being a limiting factor in oil removal. One ore volume (PV) washing solution of  $40 \text{ cm}^3$  was used to determine the residence time of surfactant at any given flow rate. For instance, maximum oil removal was achieved at  $2 \text{ cm}^3/\text{minute}$  corresponding to 20 minutes residence time. As the flow rate increases, the oil removal decreases.

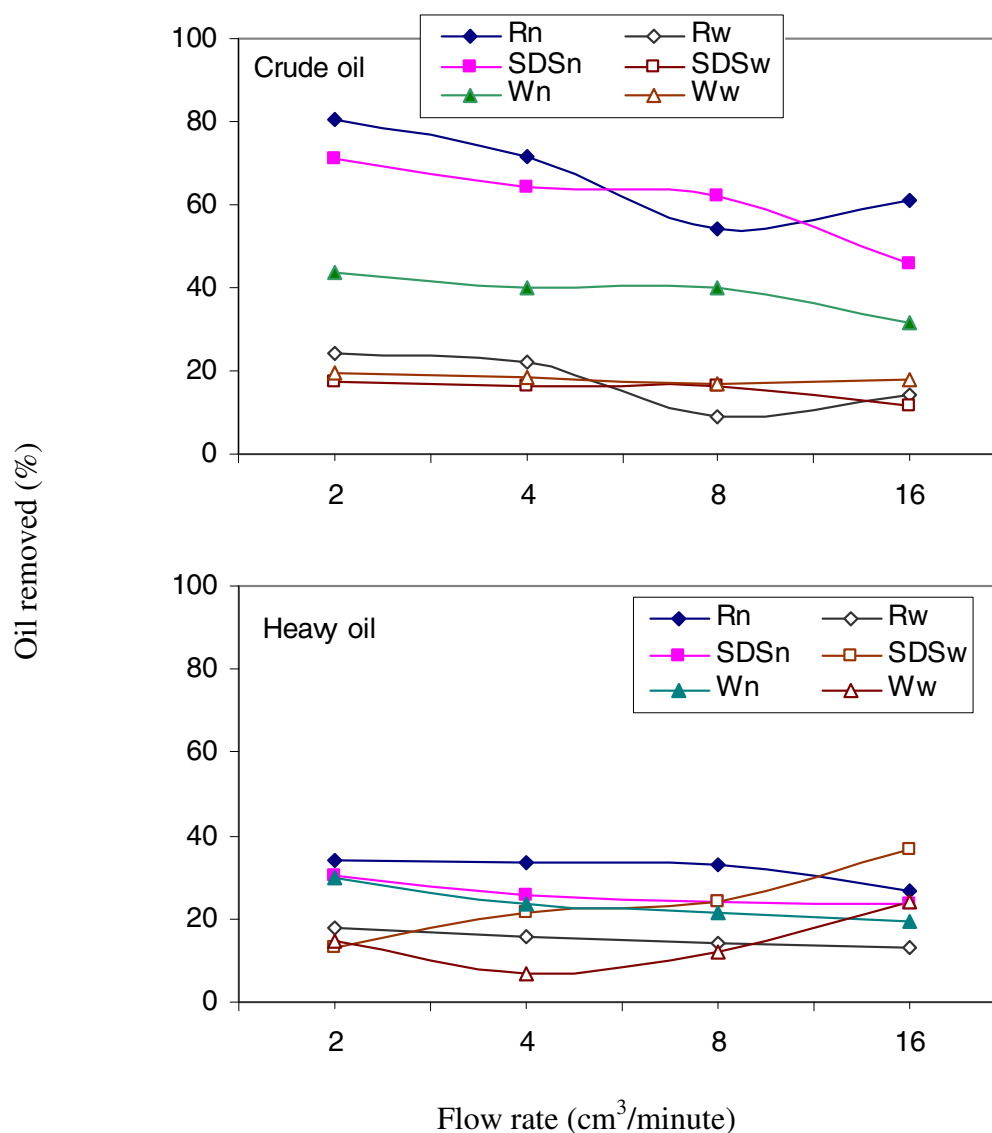


Figure 4.57. Oil removal as function of flow rate of 30PV, 0.1% mass surfactant solutions at  $20^\circ\text{C}$

The mechanical effect of flow was checked at  $32 \text{ cm}^3/\text{minute}$  for rhamnolipid solution, crude oil removal was reduced to about 48%. This indicates that as the flow rate increases, less crude oil is removed. Therefore, it was concluded that mechanical effect does not influence oil removal in the column but the longer the retention time of the

surfactants in the column will influence oil removal positively. This result may be counter to those in Section 4.2.1.5 where surfactant acts very quickly in separating oil from soil. Since the oil displaced by the surfactant solution from the soil pores can be trapped in smaller pores therefore, the displaced oil will need a longer time to travel through the soil column, however, if the density of the oil is greater than that of water, there are possibility of downward mobilization of oil.

The examination of crude and heavy oil removal from the weathered samples were within the same repeatability range, although distilled water and SDS showed inverse crude oil removal as the flow rate increases for the heavy oil. Therefore, the overall results indicate that oil removal depends more on the retention time which may contribute in the mobilization and solubilization of oil by exposing oil to the surfactants.

#### **4.5.3 Pore Volume**

This study conducted with 0.1 % mass surfactant concentration at 20<sup>0</sup>C and flow rate of 2cm<sup>3</sup>/minute indicated that crude oil removal was twice that of heavy oil. The removal of oil from the weathered samples can be assumed to be within the same range as presented in Figure 4.58. At 10 PV not much oil was removed as the surfactants were still displacing the initial 2 PV of water. When surfactant solutions fully saturated the soil column, oil removed was 54%. Rhamnolipid showed a crude oil removal of about 88% at 50 PV and then remained constant. At higher PV, rhamnolipid crude oil removal was better than SDS and distilled water. Its removal capacity is asymptote to the x-axis indicating that an increase in PV beyond 50 would not significantly enhance the oil removal. Whereas for SDS, the plot indicated that more crude oil would have been removed from the column if the PV were to be increased to above 70 PV.

Generally, SDS is expected to have a better crude oil removal than rhamnolipid, owing to the fact that rhamnolipid have a percent sorption to soil of about 75% against 33 % of SDS. The differences in oil removal between these two surfactants are insignificant. The surfactant concentration tested was low (0.1%-mass) therefore solubilization of oil was not the mechanism behind the oil removal. Hence, the major mechanism of removal was still expected to be mobilization. A comparison of interfacial tensions for the surfactants tested helps to explain the results presented in Figure 4.58. The interfacial tension of rhamnolipid –crude oil was 3.0mN/m and SDS-crude oil system was 7.5

mN/m while that of water-crude oil system was 25.mN/m. Since heavy oil and the weathered crude oil samples have high density and viscosity, it therefore needs a larger pore volume and concentration of surfactant for greater oil removal.

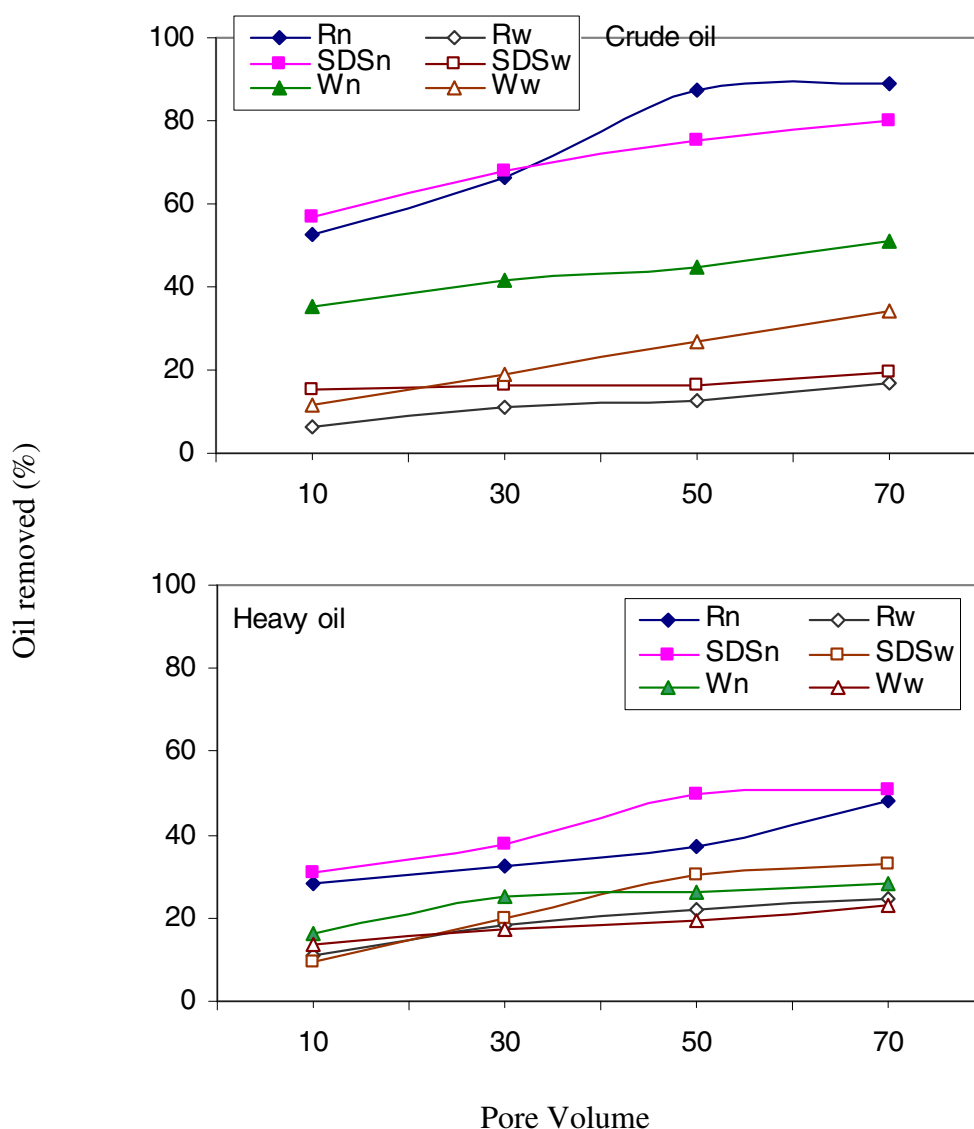


Figure 4.58. Oil removed as function of PV of washing solutions at 20°C, pumped at 2cm<sup>3</sup>/minute.

The results of this study were compared with those reported by Ang and Abdul (1991) shown in Figure 4.59. At concentration of 0.1%-mass and 10 PV, the surfactant solutions removed about 57% and 12.5% crude oil from the non-weathered and weathered soil samples compared to 32.3, 21.8 and 29.2% in 7 PV by a non-ionic surfactant (alcohol ethoxylate) at 0.5, 1.0 and 2.0%-mass concentrations respectively. The CMC of the surfactant used by Ang and Abdul (1991) is about 0.01 %-mass compared to 0.02 and 0.2 %-mass of rhamnolipid and SDS used in study. The non-ionic

surfactant used was selected from the results of a series of screening tests in Abdul et al. (1990) where it was concluded that non-ionic alcohol ethoxylate surfactant was most efficient. However, it should be kept in mind that these experiments were done in up flow mode with a fine sandy soil, whereas Ang and Abdul (1991) also used sandy soil in horizontal flow mode.

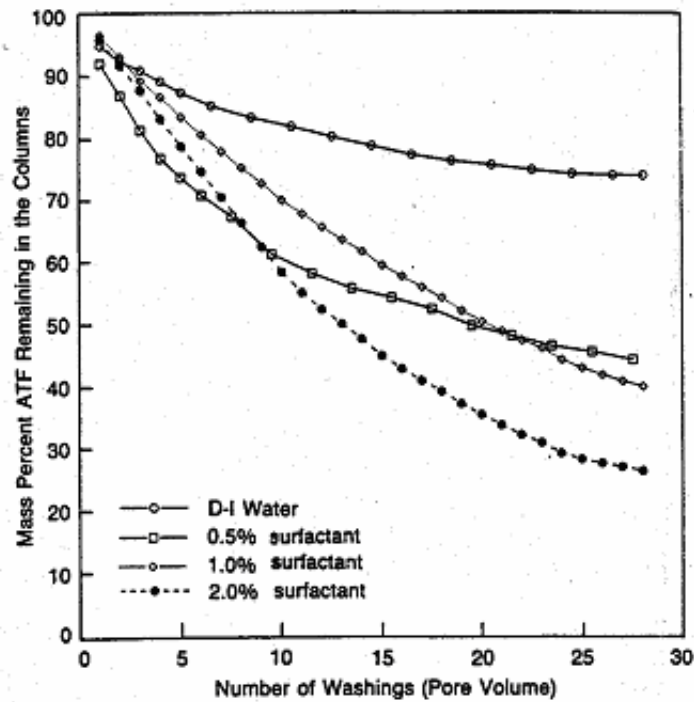


Figure 4.59. Removal of automatic transmission fluid (ATF) from contaminated soil in column. Adopted from Ang and Abdul (1991)

#### 4.5.4 Effect of temperature

Temperature affects oil viscosity; as temperature increases, viscosity of oil reduces and mobility of oil in the column increases. Also, when a surfactant is applied in soil/oil systems, the effect of temperature will invariably affect the wetting due to the increase in the mobility of the oil. In this case wetting will have a positive influence because of the direct contact of the oil and the surfactants. The ineffectiveness of surfactants during the removal of weathered crude oil contaminated soil can be related to its complex chemical nature after weathering which results in a contaminated soil with greater binding and attachment of oil to soil (Section 3.1.3.1).

At high temperature of about 35<sup>0</sup>C to 50<sup>0</sup>C, Figure 4.60 indicated that distilled water

only shows a more linear relationship with crude oil removal. However, comparing the efficiency of rhamnolipid and SDS at 20°C, results indicate that rhamnolipid and SDS show equal crude oil removal. This temperature can be justified based on cost and other treatment factors such as emission gases. Since the soil-washing process entails the reduction of possible by-products and minimization of gas emission that might occur during washing, 50°C washing pose economic and environmental disadvantages. The removal of the heavy oil was almost half the crude oil removal, therefore, confirming the adverse effect of high viscosity of oil during soil washing process.

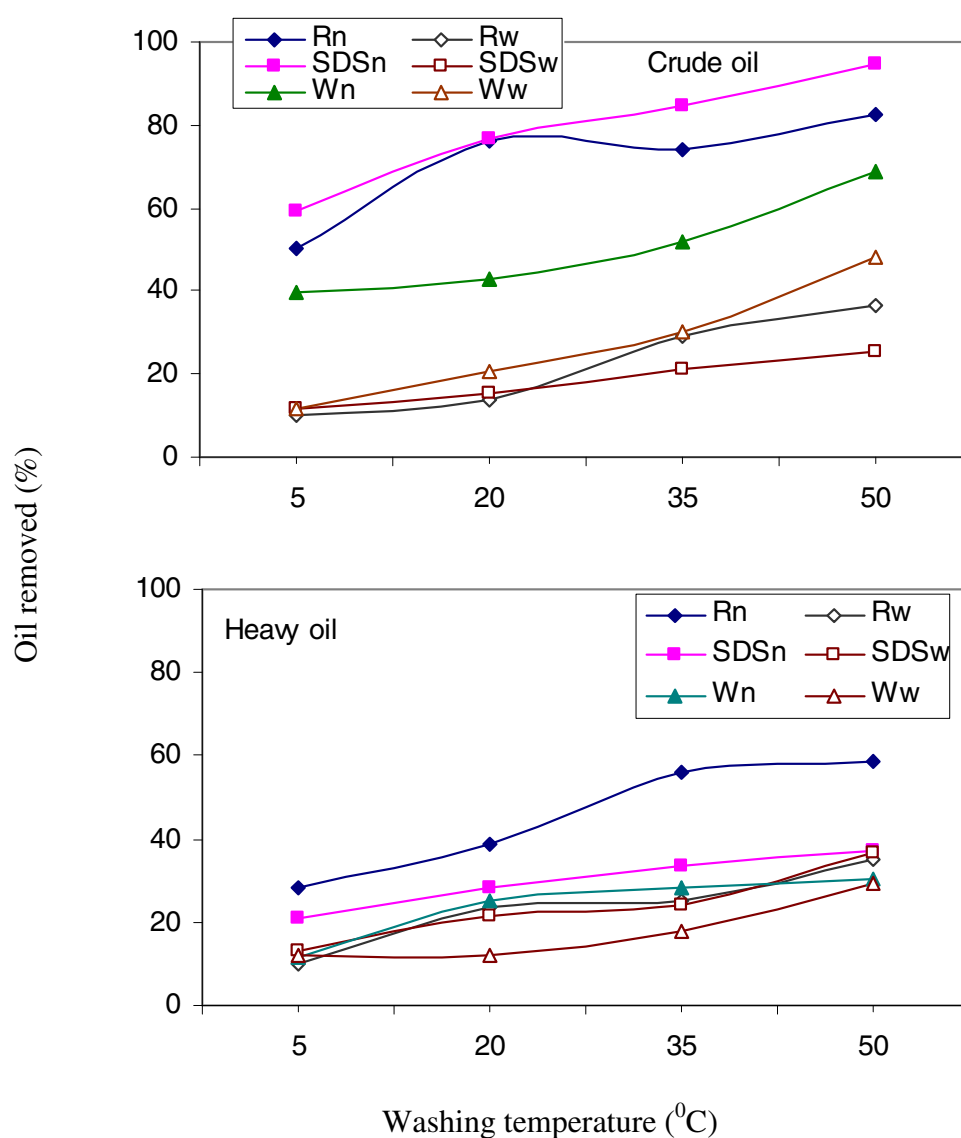


Figure 4.60. Oil removed versus temperature with 30PV of 0.1% mass surfactant solutions, pumped at 2 cm<sup>3</sup>/minute.

#### 4.5.5 Effects of oil type

The non-weathered contaminated soils washed with distilled water alone at 20°C (Figure 4.58) showed that during the PV investigation, crude oil removal increased from 35% (10 PV) to 53% (70 PV) while, the heavy oil removal from 10% (10 PV) to about 25% (70 PV). The better removal of crude oil may be attributed to the differences between the oils properties such as viscosity and density. Crude oil viscosity was less than that of the heavy oil (Section 3.1.2). Oil with high viscosity can increase the adherence or binding with soil. This may further reduce the mobility of oil thereby slowing down the oil removal process.

Therefore, due to the difference in viscosities and densities between heavy oil and water, displaced oil from soil settles down which causes the downward mobilization. More of this downward mobilization is expected in this study because of the upward flow of the washing solutions and the reduction of interfacial tension of oil-water systems. This gives the reasons why the removal of crude oil was more effective than the heavy oil during the applications of surfactant solutions.

Also the difference in density between the water and oil can aid the mobilization of oil. Because crude oil is lighter than water, the oil will be buoyed up and tend to rise vertically. However, the vertical migration of the oil due to density difference is resisted by the capillary forces which trapped the oil in the first place. In distilled water washing, the displacement of oil will be aided by the density difference.

#### **4.5.6 Sea water washing**

Results of washing of the contaminated soil using surfactant solutions prepared with seawater indicated that there was reduction in oil removal in comparison with solutions prepared with distilled water. For instance, during the concentration study for crude oil removal shown in Figure 4.61, it was observed that crude oil removal with seawater prepared solutions was about 20-30% less than that obtained in Figure 4.56. Similar observations were made for heavy oil removal, which also indicated about 10% less removal. However, the PV investigation results obtained were confusing. Although the trend in oil removal was the same using seawater and distilled water only, it was observed that crude oil removal with seawater was reduced by about 10% as PV increased from 30 to 70% in Figure 4.62, whereas heavy oil removal was enhanced by

about 10% with seawater washing.

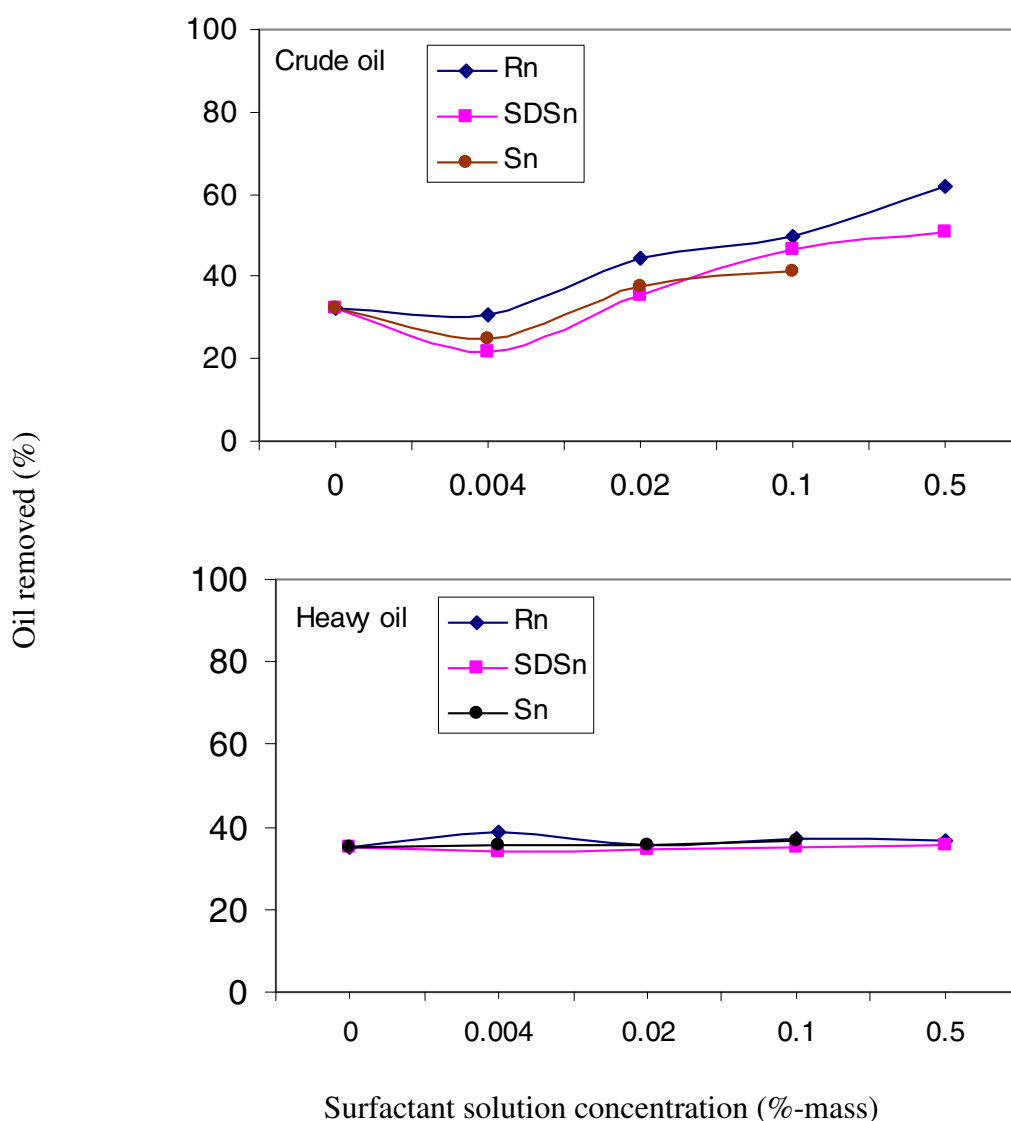


Figure 4.61. Oil removal as function of surfactant solutions concentration prepared with seawater: 30PV pumped at 2cm<sup>3</sup>/minutes at 20<sup>0</sup>C.

These results may be attributed to the resulting effect of seawater during surfactant solution preparations. It was observed that rhamnolipid precipitates in seawater and precipitation increased as concentration of rhamnolipid increased. Shiau et al. (1995) and Fountain et al. (1995) noted in their work that precipitation of surfactants may lead to loss of surfactant concentration. However, for saponin this was not observed, SDS showed crystals in seawater solutions at 0.5%-mass. But as time passed the crystals were solubilized. The disparity in the distilled and seawater oil removal may be due to the complex nature of crude oil which may have rendered the ionic strength of seawater ineffective, though seawater washing was expected to show greater oil removal due to



the electrostatic repulsion of the ionic surfactant heads. Thus, reducing the surface tensions of the surfactant solutions.

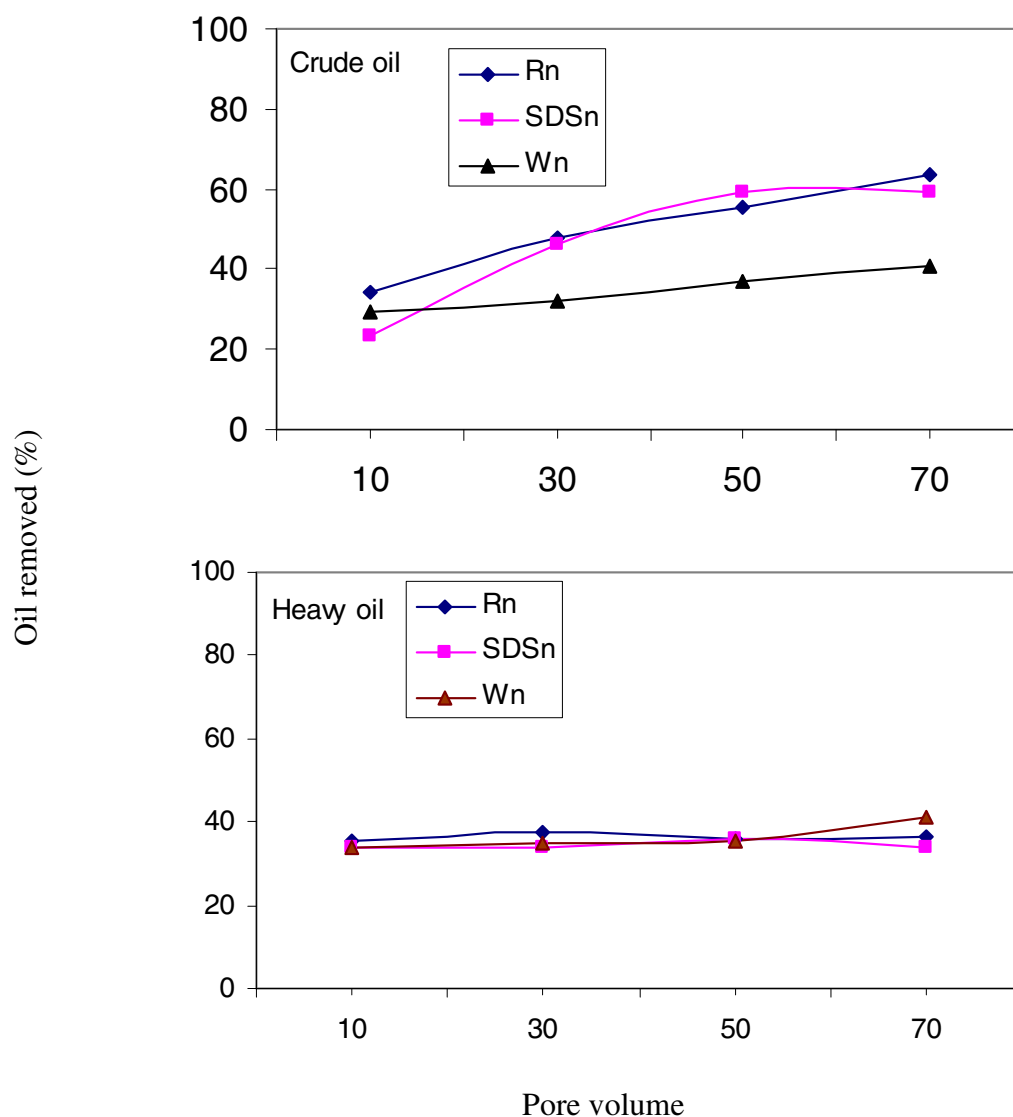


Figure 4.62. Oil removed as function of PV of seawater prepared washing solutions at 20°C, pumped at 2cm<sup>3</sup>/minute.

#### 4.5.7 Conclusions

Soil washing study was conducted in glass columns to simulate the in situ soil washing method. The removal of crude oil and heavy oil was investigated using solutions of rhamnolipid, saponin and sodium dodecyl sulfate that were prepared in either distilled water or seawater.

- Crude oil removal from the non-weathered and the weathered soil samples with

distilled water was about 40 and 20% respectively. This removal was observed to be twice the amount removed during the washing of the heavy oil contaminated soil. Rhamnolipid and saponin showed about 80 % and 60 % crude oil removal from the non-weathered samples with 0.1%-mass solutions. This concentration is about 5 fold greater than the CMC of rhamnolipid that showed the greatest oil removal.

- With the low surfactant concentrations tested, both emulsification and solubilization mechanisms were negligible. Mobilization due to the reduction of interfacial tension of oil/water system, which is responsible for the displacement of oil droplets from soil, is behind the removal of oil.
- The surfactant molecular weights and structures are in the following increasing order: SDS, Rhamnolipid, and saponin also crude oil removal was in the reverse order.
- As the flow rate increases, the oil removal decreases. Maximum oil removal was achieved at 2 cm<sup>3</sup>/minute corresponding to 20 minutes residence time. The mechanical effect of flow checked at 32 cm<sup>3</sup>/minute for rhamnolipid solution does not influence oil removal in the column but the longer retention time of the surfactants in the column will influence oil removal positively.
- At higher PV, rhamnolipid crude oil removal was better than SDS and distilled water. Its removal was asymptote to the x-axis indicating that an increase in PV beyond 50 would not significantly enhance the oil removal. Whereas SDS indicated that more crude oil would have been removed if the PV were to be increased above 70 PV.
- At high temperature of about 35<sup>0</sup>C to 50<sup>0</sup>C distilled water washing shows a more linear relationship with crude oil removal.
- Comparing the efficiency of rhamnolipid and SDS at 20<sup>0</sup>C indicate the differences in oil removal between these two surfactants were insignificant. This temperature was chosen based on cost and other treatment factors such as emission gases. Therefore, 50<sup>0</sup>C washing pose economic and environmental disadvantage.
- The removal of the heavy oil was almost half that of crude oil, which confirms the adverse effect of high viscosity of oil during soil washing process. Oil with high viscosity will increase the adherence or binding with soil. This may further reduce the mobility of oil thereby slowing down the oil removal process.
- With seawater prepared solutions, there was a reduction of about 20-30% crude oil removal in comparison with solutions prepared with distilled water. This reduction may be attributed to the resulting effect of seawater during surfactant solution

preparations such as precipitates. Precipitation of rhamnolipid increases as concentration of is increased which will lead to loss of surfactant concentration.

- The oil removal in this study was comparable with those that exist in the literature. This experiment was repeated twice, the repeatability and experimental error were found within the range  $\pm 4$  and  $\pm 3\%$ , respectively.

## **4.6 Gas Chromatograph/Mass Spectrometric analysis**

Since the process of washing crude oil contaminated soil with biosurfactants is poorly understood in terms of its chemistry, this study was undertaken. This section will present the results of crude oil removed from the non-weathered samples of Soil - 4 with rhamnolipid, saponin and SDS. The efficiency of crude oil removal process by the different surfactants was further investigated by carrying out a gas chromatography-mass spectrometry (GC/MS) analysis of the washed soil samples to determine if there is a preferential removal of specific crude oil components from soil. In particular, the relative removal of the aliphatic versus, the more toxic, aromatic compounds.

As the technique of soil washing is still a developing remediation technology for the treatment of crude oil contaminated soil, the use of GC/MS to study the detailed hydrocarbon compositions will enhance the selection of surfactants for crude oil contaminated sites. This will be possible if the both the physical and chemical characteristics of the oil are known.

### **4.6.1 Soil washing**

The percentage crude oil removed from the weathered soil (Soil – 4) after washing with the surfactant solutions (rhamnolipid, saponin and SDS) in test tubes, shows that SDS produced the maximum crude oil removal (46.09%) followed by rhamnolipid (43.93%) and saponin (26.83 %). As all the surfactant solutions showed crude oil removal less than 50% with 20 cm<sup>3</sup> 0.1%-mass solutions, it was assumed that this low removal was due to the effect of weathering of the contaminated soil which had already removed the most volatile hydrocarbons and concentrated the higher molecular weight, more complex materials (aromatics, asphaltenes, and non-organics) that remained. Therefore, a GC study was conducted for each of the crude oil/n-hexane extracts to observe the trend of the hydrocarbons remaining in the washed soil and the results compared with Figure 3.7c (weathered crude oil contaminated soil).

#### 4.6.2 GC analysis of the washed contaminated soil

After washing the crude oil contaminated soil with the different surfactant solutions, the oil remaining on the soil was extracted using n-hexane. The extracts were then subjected to gas chromatography and the results are presented in Figure 4.63, 4.64 and 4.65 for rhamnolipid, saponin and SDS respectively. The chromatogram shown in Figure 3.7c was used as a control to check the extent of crude oil removal from soil by the different surfactants.

It is observed in the GC chromatograms shown in Figure 3.7c, Figure 4.63, to 4.65 that the surfactant solution further reduces the levels of hydrocarbons compared to those in the control shown in Figure 3.7c. Saponin (Figure 4.64) produced a greater reduction of hydrocarbons in the range of C<sub>10</sub> to C<sub>18</sub> followed by rhamnolipid shown in Figure 4.63 and then SDS shown in Figure 4.65. The loss of hydrocarbons indicated in Figure 4.63 to 4.65 contrasts with the percentages of crude oil removed from the soil (Section 4.6.1). For example SDS, which has removed almost twice the amount of crude oil from the soil compared to saponin, showed less reduction of n-alkanes in the range C<sub>10</sub> to C<sub>18</sub> when compared to the control (compare Figure 3.7c). A detailed mass spectrometric (MS) study was therefore conducted to investigate if there are preferences in crude oil component removal from soil with the different surfactant solutions.

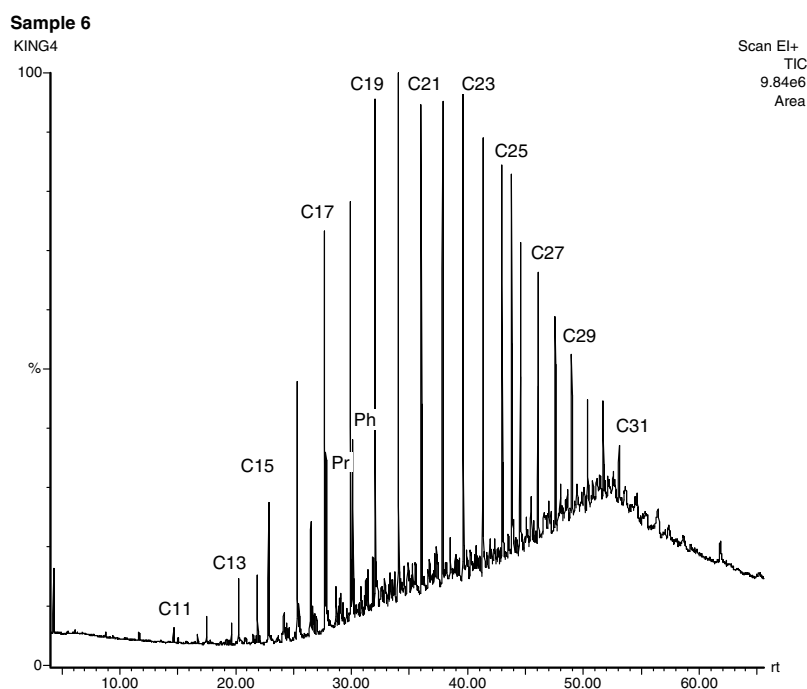


Figure 4.63. GC/MS chromatogram of weathered Ekofisk crude oil contaminated soil washed with 0.1%-mass rhamnolipid solution

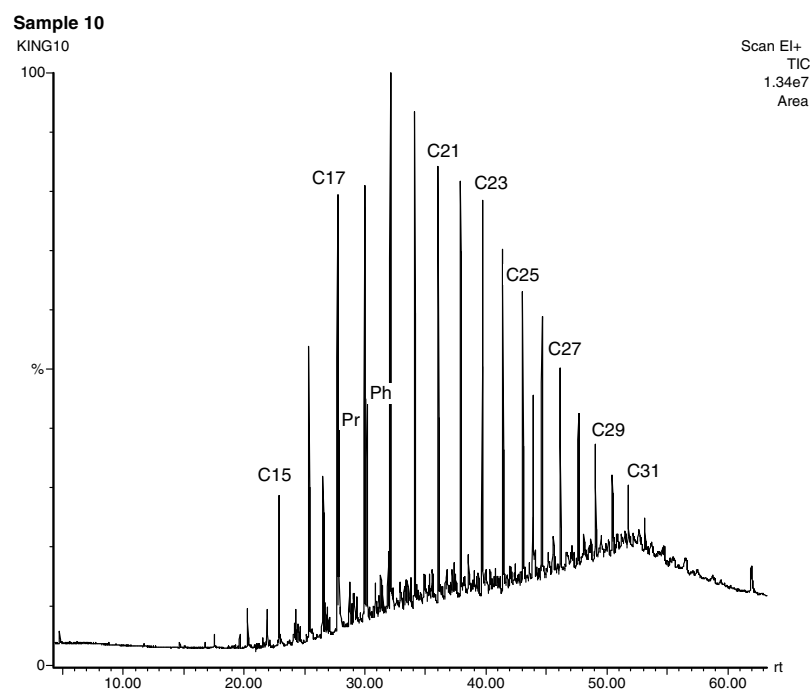


Figure 4.64. GC/MS chromatogram of weathered Ekofisk crude oil contaminated soil washed with 0.1%-mass saponin solution.

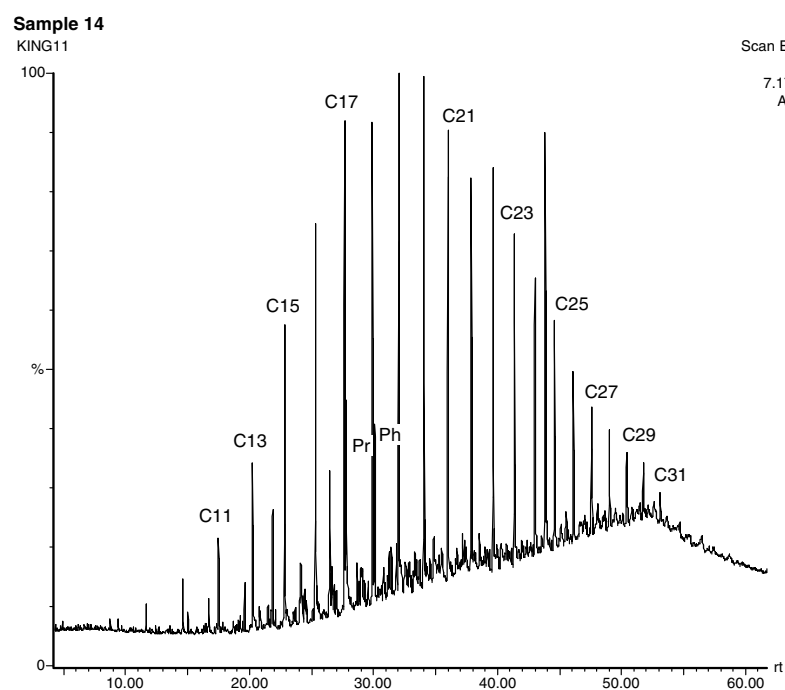


Figure 4.65. GC/MS chromatogram of weathered Ekofisk crude oil contaminated soil washed with 0.1%-mass SDS solution

### 4.6.3 GC/MS analysis of aromatic and aliphatic hydrocarbon

A GC/MS study was conducted with the n-hexane extract from the contaminated soils. This study was used to observe if there is a preferential removal of crude oil components, such as the aliphatic and the aromatic hydrocarbons, from the contaminated soil. The results of these studies for the control are presented in Figure 4.66 to Figure 4.68, while those for the surfactant solutions are shown in Appendix A2. To enable a quantitative comparison of the relative removal of aliphatic and aromatic compounds from the soil to be made, the areas of the peaks under the chromatograms were determined. The area under the chromatogram within the hydrocarbon range of C<sub>10</sub> to C<sub>35</sub> was determined for the aliphatic hydrocarbons in Figure 3.7c, Figure 4.63 to 4.65. For the aromatic hydrocarbons – naphthalenes, phenanthrenes and dibenzothiophenes (NPDs), the chromatograms shown in Figure 4.66 to 4.68 were used. The analysis of the results of the area under the chromatogram are summarised in Table 4.6.

Table 4.6. Area of the chromatogram of crude oil components remaining in soil

Samples	Total aromatic	Aliphatic	a/b x 100	Control/ surfactant	Control/ surfactant
	(a)	(b)		(a)	(b)
Control	139 797	2 662 453	5.25	1	1
Rhamnolipid	101 542	996 600	10.19	1.38	2.67
Saponin	67 894	1 306 917	5.20	2.06	2.03
SDS	133 566	993 251	13.45	1.05	2.68

Using the ratio of total aromatics (a) / total aliphatics (b), that is, (a/bx100) = 5.25 for the control sample, a hypothesis was set up to understand if there is preference for the removal of crude oil components from the contaminated soil.

Hypothesis 1: If  $a/b \times 100 < 5.25$  = More aromatics are removed

Hypothesis 2: If  $a/b \times 100 > 5.25$  = More aliphatics are removed

In Table 4.6, it can be seen that there was no preferential removal of the aromatic compared to the aliphatic hydrocarbon fractions using saponin. Saponin showed

approximately the same a/b with the control sample. For rhamnolipid and SDS, there was a preference for the removal of aliphatic hydrocarbon from soil over the aromatic hydrocarbons. This could be seen from Table 4.6 since a/b for SDS and rhamnolipid are greater than the control ( $a/b \times 100 = 5.25$ ), which agrees with hypothesis 2. This analysis suggests that the reason why rhamnolipid and SDS have greater crude oil removal from soil over saponin (Section 4.6.1) is that they remove a greater proportion of the aliphatic hydrocarbons from the oil.

The analysis in Table 4.6 also indicated that surfactants of higher molecular weights and more complex structures such as saponin might remove more aromatic hydrocarbon than the aliphatic hydrocarbons in comparison to rhamnolipid and SDS. The aromatic hydrocarbons remaining in the washed soil using saponin were about half the concentration of those using rhamnolipid and SDS. Thus, further analysis was carried out using the mass chromatograms shown in Figure 4.66 to 4.68, to investigate the individual aromatic hydrocarbons that remain in the washed soil.

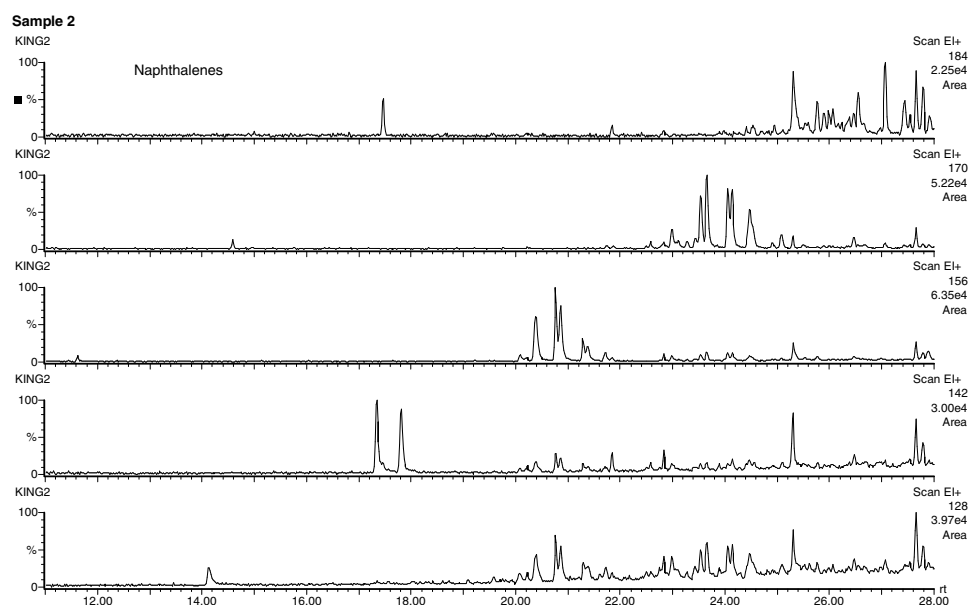


Figure 4.66. GC/MS chromatograms of control sample at m/z 128, 142, 156, 170 and 184 for naphthalene aromatic hydrocarbon



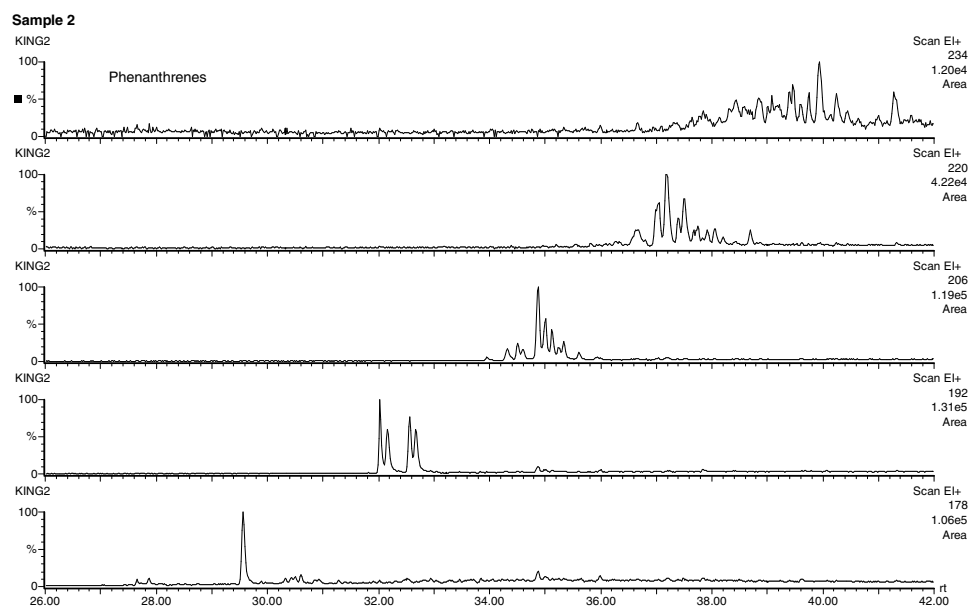


Figure 4.67. GC/MS chromatograms of control sample at m/z 178, 192, 206, 220 and 234 for phenanthrenes aromatic hydrocarbon

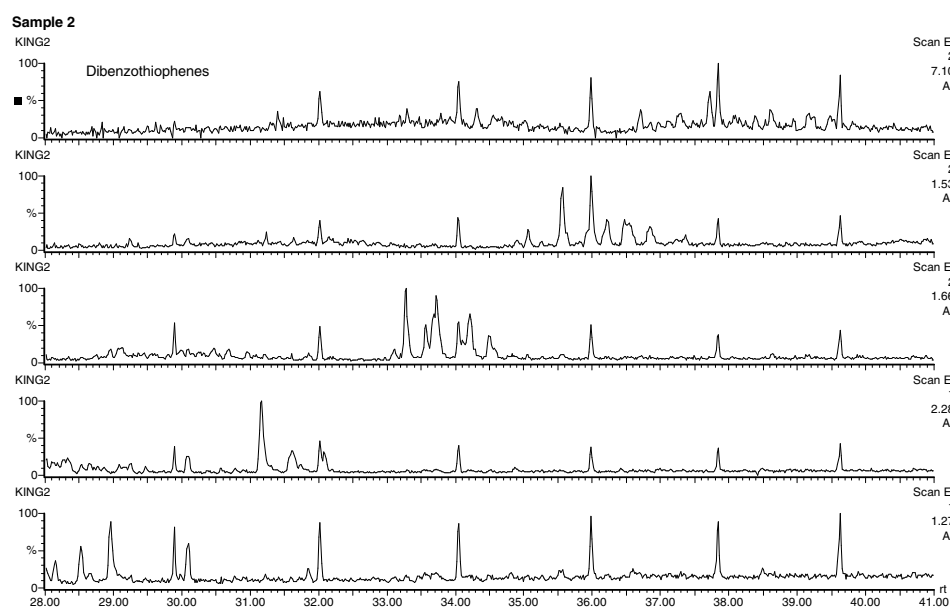


Figure 4.68. GC/MS chromatograms of control sample at m/z 184, 198, 212, 226 and 240 for dibenzothiophenes aromatic hydrocarbon

#### 4.6.4 The aliphatic hydrocarbons

To observe the relative concentrations of n-alkanes remaining in the washed soil following the application of the three different surfactants, the area of each of the normal alkanes in Figure 3.7c, Figure 4.63, to 4.65 was normalised to the area of the

nC<sub>25</sub> alkane. The normalised distributions are presented in bar charts in Figure 4.69.

Up to C<sub>15</sub>, the saponin removed the greatest proportion of n-alkanes and SDS the least relative to the control. From C<sub>16</sub> to C<sub>21</sub> the rhamnolipid removed the greatest proportion of n-alkanes and, again, SDS the least. Above C<sub>22</sub> the distributions were similar. The results suggest that the different surfactants will preferentially remove different amounts of the same alkanes.

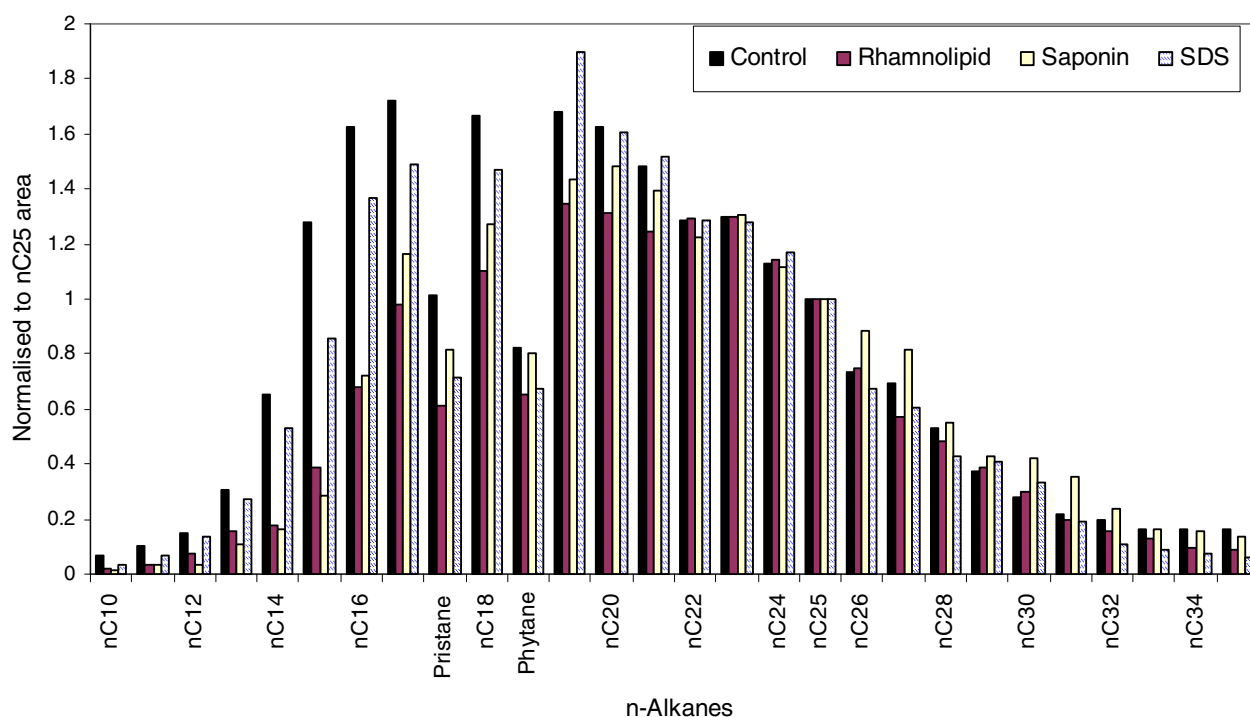


Figure 4.69. Relative distribution of n-alkanes: normalised concentration relative to n-C<sub>25</sub>

#### 4.6.5 The aromatic hydrocarbons

To understand the extent of aromatic hydrocarbon removal from the soil, analysis of the individual aromatic compounds (Naphthalenes, Phenanthrenes, Dibenzothiophenes) was investigated. The relative concentrations of the aromatic compounds remaining in the washed soil as measured by their areas are shown in Figure 4.70.

These results show that the phenanthrenes are the most abundant aromatic in the control followed by the naphthalenes and then the dibenzothiophenes. None of the surfactants remove a significant amount of dibenzothiophenes compared to the control. Both

Rhamnolipid and Saponin remove a significant proportion of the naphthalenes whereas SDS removes only a small amount. Saponin removes the greatest proportion of phenanthrenes and SDS the least. This data shows that the different surfactants will preferentially remove different aromatic compounds by different amounts.

Interestingly the area of total aromatics for the SDS is similar to the control (Table 4.6). However, the area of the aliphatics is 2.7 x lower. This suggests that the majority of oil components washed out of the soil by SDS are aliphatics. By contrast, the Saponin removes aromatics and aliphatics in equal proportions. Rhamnolipid removes equal amounts of naphthalenes and dibenzothiophenes to Saponin but is not as efficient at removing the phenanthrenes. However, Table 4.6 indicates that Rhamnolipid removes a much greater proportion of aliphatics than aromatics. The differing efficiency with which these surfactants remove crude oil components are important environmentally, due to the higher toxicity of aromatic versus the aliphatic compounds. In addition, the aromatics tend to be more recalcitrant and therefore their removal from soil is highly desirable. By contrast, residual aliphatic components should degrade naturally.

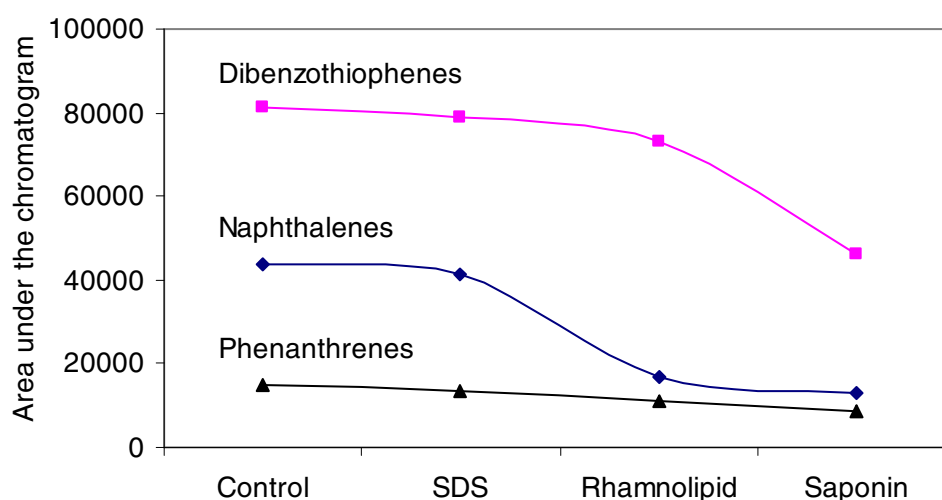


Figure 4.70. Area of the GC/MS chromatogram of aromatic hydrocarbon compound remaining in soil after washing

#### 4.6.6 Conclusions

These results provide important information for the selection of surfactants used to remove crude oil from contaminated soils. This study shows that biosurfactants can be

equally as efficient at removing oil from soil as synthetic surfactants. Further, biosurfactants can preferentially remove certain aromatic groups, which may be desirable for more rapid soil remediation.

The relative loss of the different hydrocarbon components through the soil washing process are summarised below.

- Rhamnolipid and SDS are the most, and equally, efficient at removing crude oil from soil, while saponin is the least efficient.
- Rhamnolipid and SDS remove a relatively greater proportion of the aliphatic components. Saponin removes aliphatic and aromatic components in equal proportions.
- Rhamnolipid and Saponin are more efficient at removing the naphthalenes than SDS. Saponin is the most efficient at removing the phenanthrenes.

## 4.7 Optimization of crude oil removal

In order to determine the best washing conditions, an optimisation of the soil washing process was conducted using Taguchi experimental design method in the test tube washing setting. The optimum conditions were determined for the non-weathered crude oil contaminated sample of Soil – 4 with all the biosurfactant solutions. The optimum values obtained through experimental runs were used to predict crude oil removed at three confidence intervals (90%, 95% and 99%). The results of crude oil removal obtained through experimental runs and predictions were compared and used to assess the robustness of the washing method.

Results showed that the optimum washing conditions for temperature and time were found to be 50°C and 10 minutes for all the surfactant solutions tested. The other parameters show optimum values at different points for different surfactants. However, SDS, rhamnolipid and saponin show an oil removal of greater than 79%. The washing method was found to be more stable at error of  $\pm 1\%$  for all the surfactant solutions except aescin and lecithin.

### 4.7.1 Optimum crude oil removal

As this washing was carried out with the Taguchi method, crude oil removed by any parameter was influenced by other parameters. Thus, the results of this study will be explained based on the Taguchi method. Since it is cumbersome to deduce an experimental plan as presented in Table 3.33 that results in graphs Figure 4.71a-e, these figures will be explained by giving examples. For instance, Figure 4.71a shows the variation of performance statistics with temperature. To determine the experimental conditions of rhamnolipid at level 1 (that is, at 5°C) with the average performance statistics value of 26.34, from Table 3.33 the experiments with temperature level 1 are with experimental numbers 1, 2, 3, and 4. The performance statistics at this temperature is the average of these four experiments. Experimental conditions for the second data point are experiments with experimental numbers 5, 6, 7 and 8 and so on. The performance statistics for each surfactant were plotted against the investigated parameters and the optimum points were determined for each surfactant.

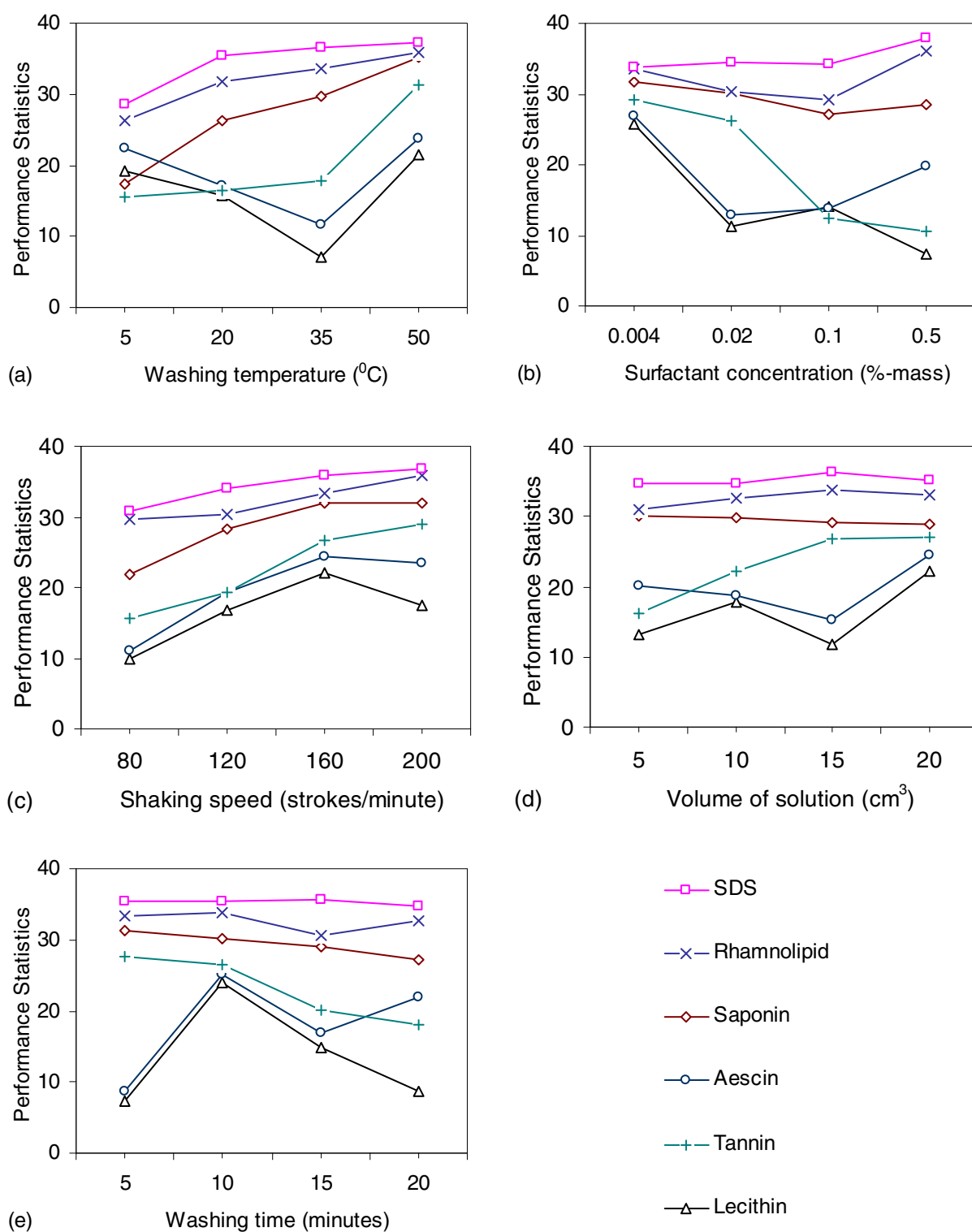


Figure 4.71a-e. Effect of parameter on performance statistic

The maximum point on the curve was chosen for each surfactant as the optimum point. In some cases, the lower level points were chosen when the performance statistics were within the same range of values. Hence, optimum washing conditions determined are shown in Table 4.7. However, after evaluating Equation 3.19, temperature was found to

be the most influential parameter for all biosurfactants, except lecithin, which indicates solution concentration to be its most influential parameter. However, the least influential parameters were found to be washing time and volume of solutions. The order of the graphs in Figure 4.71a-e is according to the degree of the average influence of parameters on crude oil removal from soil. This was determined by finding the range between the largest and the lowest value of crude oil removal for each surfactant solution after evaluating Equation 3.19.

Table 4.7. Optimum conditions

Surfactant solutions	Temperature ( $^{\circ}\text{C}$ )	Conc. of solution (%-mass)	Vol. of solution ( $\text{cm}^3$ )	Shaking speed (strokes/minute)	Time (minutes)
Aescin	50	0.004	20	160	10
Lecithin	50	0.004	15	200	10
Rhamnolipid	50	0.5	15	200	10
Saponin	50	0.004	10	200	10
SDS	50	0.5	15	160	10
Tannin	50	0.004	15	200	10

#### 4.7.2 Predicted crude oil removal

Considering the optimum conditions obtained from Table 4.7, careful consideration of the experimental plan in Table 3.33 can explain that the experiment corresponding to the optimum value may not have been carried out during the whole washing process. This is applicable for all the surfactant solutions except aescin that corresponds to experiment number 16. With equations 4, 5 and 6, crude oil removed was predicted using the optimum conditions at the following confidence limit 90%, 95% and 99%. The predicted crude oil removal was confirmed by carrying out a laboratory experiment twice at the optimum washing conditions shown in Table 4.7. The average result obtained from the laboratory confirmed experiment is presented in the second column of Table 4.8.

The value of the predicted crude oil removal shown in the third column of Table 5.2 can be obtained for any confidence intervals by inserting the value of  $R_i$ , that is,  $R_{90\%} = \pm 13.34$ ,  $R_{95\%} = \pm 16.23$  and  $R_{99\%} = \pm 22.45$ . For instance, Rhamnolipid predicted crude

oil removal at 90% would be within the range 79.16% - 105.84%. The negative predicted crude oil removal for aescin and lecithin indicates that over all the experimental runs, crude oil removal in some of the levels were zero. This may be due to their nature observed earlier on which also occur using the Taguchi method as observed with 0.5%-mass lecithin solution, and during 5 minutes washing of aescin.

Table 4.8. Oil removal at optimum conditions

Surfactants	Crude oil removed (%)	
	Experiment	Predicted
Aescin	30.32152	$4.4 \pm R_i$
Lecithin	9.645246	$3.3 \pm R_i$
Rhamnolipid	79.87805	$92.5 \pm R_i$
Saponin	80.73725	$92.9 \pm R_i$
SDS	96.61863	$94.9 \pm R_i$
Tannin	32.92684	$45.8 \pm R_i$

Although, aescin confirmatory experimental crude oil removal corresponds to the value of about 31% obtained during the experiment, (experiment number 16 from Table 3.33). The removal is not within the range predicted for the three confidence intervals. This implies that its removal has a large variation and is not stable. For the other four surfactants, their confirmed experimental crude oil removed from soil was within the predicted limits indicating process stability and robustness. The range of predicted crude oil removal at  $\pm 1\%$  error levels was greater than those of  $\pm 5\%$  and  $10\%$  error levels. Thus, with Taguchi experimental method higher process performance was obtained at low error levels indicating stability within the range of  $\pm 1\%$ .

### 4.7.3 Conclusions

The Taguchi experimental design method was used to assess the robustness or stability and reproducibility of the experimental method for possible field scale applications.

- Results gained from these studies indicated that temperature and concentrations of surfactant solutions were the most influential parameters.



- With the Taguchi method the removal of crude oil with rhamnolipid and saponin was observed to be about 80%.
- The confirmatory experiment and the predicted crude oil removal showed that the washing method was stable for all the biosurfactant solutions except aescin and lecithin which show predicted crude oil removal out of range.
- As error level is increased from  $\pm 1\%$  to  $\pm 10\%$ , stability of the washing method reduces.
- Although the cost analysis is not given, this work suggested a field scale investigation to assess the surfactants performances in removing crude oil from both weathered and non-weathered contaminated soil samples.

## **5 Conclusions and Recommendations**

### **5.1 Conclusions**

The removal of crude oil and heavy oil from contaminated soil of different particle size fractions have been carried out through various soil washing settings using aqueous surfactant solutions (prepared in distilled water and seawater), distilled water and seawater only. The biosurfactant tested were aescin, lecithin, saponin, rhamnolipid and tannin, and a synthetic surfactant sodium dodecyl sulfate was used for comparison. Effects of different parameters such as temperature, volume of surfactant solution, concentration of surfactant solutions, volume of washing solution, pore volume of surfactant, flow rate, and soil fractions were investigated. The following conclusions can be drawn from this study.

#### **5.1.1 Soil characterizations**

- The value of the water content (0.54%) in soil did not influence the washing solutions performance in oil removal either by contributing to an increase in the solution volume, which may lead to the reduction of concentration of surfactant solutions or have any significant effect on extraction of oil from soil using n-hexane.
- Texturally, Soil – 1 with more than 60% particles  $\leq 0.002$  mm was considered as clay soil, Soil – 2 with more than 60% particle  $\leq 0.06$  mm as silt soil, Soil – 3 as fine sand ( $\leq 2$  mm), Soil – 4 as coarse sand ( $\leq 4$  mm) and Soil – 5 as gravels (2-4 mm).
- The decreased in the porosity of the contaminated soils with respect to the uncontaminated ones shows the adverse affects of oil on soils' mechanical and physical properties. This can contribute to the reduction in permeability and poor aeration of soil due to the displacement of soil pores with oil. The soil porosity value was used to estimate the pore volume of surfactant during the soil washing in column setting.
- The flow of water in the soil column was stable, no air entrapment and settling or washing out of soil particles during the permeability study. The coefficient of permeability obtained was within the range of 0.01-1.00 cm/sec for coarse and

medium sand, which is an indication that the soil permeability will control the mobility of surfactants and removed oil in soil during the soil column washing.

- All the soil samples showed a neutral pH except Soil – 2 with pH of 6.29. The application of surfactant solutions in soil washing will not influenced the acidity or alkalinity of the soil samples. This will be advantageous for the soil washing studies since one of its main objectives is to investigate the performances of the surfactant solutions at their natural properties such as pH.
- Since the pH of the surfactant solution was within the pH of the soil samples, this eliminates the possibility of accelerating the soil cation exchange capacity (CEC), if the pH of surfactant solution used is much greater. Oil tends to bind with soil that have greater amount of CEC therefore the knowledge of CEC was useful in developing a treatment procedure for the different soil fractions.

### **5.1.2 Oil contaminated soils**

- The soil contamination process shows that as the soil particle size increased, less oil was needed to saturate the soil. Oil saturation with soil was limited to the quantity of oil that could withstand the total mass of soil without draining.
- Since, n-hexane extraction more than 97 % of crude oil was removed from soil, the disparity of initially oil used for soil contamination and those observed after the contamination was due to the loss of materials during the contamination process.
- During weathering, the volatile components of oil were lost due to evaporation within the first 24 hours, thereafter, the mass reduction of the contaminated soil was not changing but the proportion of higher molecular weight components in the oil increase due to the concentration of components in the oil such as sulphur, asphaltenes and metals which result to a contaminated soil with a higher density and viscosity.
- The GC study showed the disparity in oil lost in the fresh oil, non-weathered and weathered soil samples. After weathering, carbon numbers less than C<sub>16</sub> were lost and the peak of the hydrocarbon was normalized with C<sub>17</sub>. The based of the chromatogram was noticed to have rise leading to the formation of the unresolved complex mixture (UCM). The resulting oil in the weathered soil samples adhered and binds more in the soil surfaces than in the non-weathered samples. Therefore, weathering effect was noted to be a limiting factor in the oil removal from soil.
- With the dominance of UCM and very small amount of resolved peaks being

detected with the heavy oil, its removal from contaminated soil seems to be difficult when compared with crude oil that have less UCM.

### **5.1.3 Surfactant surface and interfacial tension**

- The surface tension measurement for distilled water prepared solutions indicated that the CMC of rhamnolipid, aescin saponin, lecithin, tannin and SDS occur at 0.02, 0.1, 0.1, 0.4, 0.008 and 0.2 %-mass solution respectively, while those prepared in seawater have a CMC of 0.008, 0.20, 0.08, 0.40, 0.01 and 0.10 %-mass for rhamnolipid, aescin saponin, lecithin, tannin and SDS respectively. The CMC of the surfactant solution is a good indicator for surfactant effectiveness in removing oil from a contaminated soil. Surfactants with a low CMC are expected to have greater oil removal.
- The interfacial tension between crude oil and distilled water was measured as 25 mN/m, but was reduced for the crude oil-surfactant systems to a value corresponding to the CMC of the surfactant solutions.
- The reduction of interfacial tension indicates the ability of surfactants to separate oil from soil. The interfacial tension obtained were not ultra low ( $<1$  mN/m), however it will lead to the reduction of the capillary force holding oil and soil together which result to the mobilization of oil.
- Rhamnolipid and tannin would show more potential in oil removal from soil than the other surfactant solutions. Their interfacial tension with crude oil was about 4.5 mN/m while lecithin shows less potential in comparison with the other biosurfactants.

### **5.1.4 Surfactant foaming**

- Saponin has greater initial foaming ability than the other surfactant solutions. However, saponin foams was not as stable as those of SDS after 5 minutes.
- SDS foaming was more stable over the tested range of concentrations, followed by aescin and then saponin. Foaming is a good indication of surfactants' detergency, which shows surfactant ability to removed oil from soil. Surfactant foaming may be wanted during oil removal with air sparging reactor however it will be undesirable in soil column washing.

### 5.1.5 Surfactant sorption to soil

- Surfactant with less sorption in soil have greater tendency in oil removing. Sorption in soil will lead to the lost of surfactant monomers which may contributes to less formation of micelles.
- When surfactant have a low CMC get in contact with soil, as the concentration of the surfactant solution is increased beyond the CMC, the surfactant monomers may form more micelles which will replaced those adsorbed by soil. Thus, surfactants with low CMC, even with high sorption to soil have a better tendency in oil removal. This will be possible if the solution concentrations employed during soil washing is far greater than the CMC.

### 5.1.6 Surfactant emulsification

- Due to its low asphathenes content (0.03 %-mass) of Ekofisk crude oil, could not form emulsions in the absence of surfactants however, as the surfactant solutions were added mesostable emulsions were formed.
- The emulsions formed were easily diluted in water, while it could not dilute in crude oil thus emulsions were of oil-in-water type. Therefore, the surfactants hydrophilic–lipophilic balance were within the range of 8–18. The formation of o/w emulsions will favour the application of aqueous surfactant solutions in oil removal.
- The emulsification effectiveness of surfactant was considered to be those that shows greater emulsions phase only and/or water phase with less crude oil phase, as solution concentrations and surfactant solution/crude oil ratio increases.
- The entire three phases may be attribute to the bulky molecular structure of the tannin, saponin, lecithin and aescin. Surfactants with bulky molecular structures change the size and shape of micelles as the concentration increases leading to instability of surfactant solution.
- Lecithin has a bulky molecular structure; its solutions were also noted to be more viscous than the other surfactants tested. In soil washing lecithin interfacial contact with crude oil might not be as good as the other surfactants. Therefore, the formation of excess crude oil phase observed will not favour its oil removal effectiveness.
- Emulsions will aid in the soil treatment process by increasing the surface area between the surfactant and oil (if the interfacial tension is ultra low, that is less than

1 mN/m). This allows the surfactant to react easier in absorbing the non-polar oil into the interior of the surfactants micelles, thus increasing the oil solubility. If the emulsion is carried easily by the surfactant, it will aid in the removal of the micelles-oil mixture from the soil and surfactant.

- Emulsion will hinder the progression of oil removal from soil if the thickness of the emulsion layer becomes too thick. This will act as a barrier that isolates the oil from the surfactant solutions. It also can clog the pore spaces of soils thus preventing the rapid removal of micelles-oil mixture.

#### **5.1.7 Surfactant solubilization**

- The crude oil solubilization in distilled water and seawater was 1.5434 and 18.36 mg/liter respectively. The solubilization effectiveness of crude oil into the surfactant solution micelles was assumed to occur above the surfactant solution CMC.
- SDS has the maximum solubility of about 180 mg/liter (0.11%) of the crude oil in seawater. Rhamnolipid and SDS also showed greater solubilization of crude oil in the seawater than that in distilled water. The salts in seawater decrease the repulsion between similar charged ions in the surfactant head group.

#### **5.1.8 Surfactant precipitation**

- Seawater did not reduce the concentrations of saponin and SDS. However, SDS solubility was not as fast as when prepared in distilled water. SDS solutions coalesce and appear turbid, after about two hours the solution becomes clear
- For rhamnolipid, there was settling of materials at the bottom of the volumetric cylinder, the precipitation of rhamnolipid may lead to the lost of surfactant micelles.
- The knowledge of precipitation of rhamnolipid gives an idea in selecting washing time and flow rate of solutions during column soil washing.

#### **5.1.9 Soil washing: screening of biosurfactants in test tube**

The following conclusions were drawn from study on biosurfactants removal of Ekofisk crude oil from the non-weathered samples of Soil –4.

- Rhamnolipid and SDS were effective in removing up to 80 % crude oil from the contaminated soil over the range of parameters tested. In most cases, rhamnolipid

and SDS crude oil removal were within the same experimental repeatability range of  $\pm 6\%$ .

- Maximum crude oil removal was achieved at 50°C for all the surfactants except lecithin that had a maximum crude oil removal of only 42% with 0.004%-mass solution.
- Crude oil removal from soil was due to mobilization of oil. Solubilisation does not have any effect in oil removal due to the low crude oil solubilization of 0.11%.
- Apart from rhamnolipid, the performance of water alone was equally good as those of the other biosurfactant solutions during blending. The approach of blending may be cost effective.
- The effect of washing temperature showed a significant removal of crude oil, more so than shaking speed, volume and concentration of surfactant solutions, and washing time. The effect of washing time however was less influential in crude oil removal because most biosurfactant solutions showed differences in crude oil removal of 30% between the first and fourth parameter levels.
- Therefore the results obtained during the screening study were used to design a soil washing process for weathered crude oil contaminated soils in tests.

#### **5.1.10 Soil washing: different soil fractions in test tube**

Rhamnolipid, SDS and distilled water were employed in this study to remove crude oil from different weathered and non-weathered contaminated soil samples. The effects of different parameters such as washing temperature, volume and concentration of solutions, shaking speed and washing time was investigated. The following conclusions can be made from the study:

- Notwithstanding the differences in the physio-chemical properties of surfactant solutions such as sorption to soil, solubilization, surface and interfacial tension, the removal of crude oil from the weathered and non-weathered soil samples using rhamnolipid and SDS was within the same experimental repeatability range  $\pm 6\%$ .
- The surfactants enhancement of crude oil removal was better for the non-weathered soil samples than for the weathered soil samples. This was due to the resulting complex nature of the weathered contaminated soil that contained oil with higher molecular weight.
- The overall crude oil removal from the non-weathered soil samples were in the following descending order: Soil – 2, Soil – 3, Soil – 4 and Soil – 5, whereas the

reverse (Soil – 5, Soil – 4, Soil – 3 and Soil – 2) was true for the weathered samples. This was possible since the non-weathered soil samples are freshly contaminated thus, the binding of oil to soil will be less coupled with the large surface area of the fine soil samples. For the weathered samples, the oil content in soil fractions was less with larger soil fractions therefore fast desorption of oil from soil was achieved.

- The results obtained throughout this study could be generalized for other non-aqueous phase liquids such as heavy oil with density greater than water. The data obtained was used to design soil washing process for the other settings (such as stirred tank, air sparging and assisted stirred tank reactor and column) for washing large quantity of contaminated soils.

#### **5.1.11 Soil washing: stirred tank reactor**

Soil washing in stirred tank reactor was examined to mimic the ex-situ technique. This study employed two contaminants (crude oil and heavy oil) and the amount of contaminated soil washed was scale up to 10 g. With emphasis on crude oil, the oil removal from the different soil fractions (Soil – 1, Soil – 3, Soil – 4 and Soil – 5) were used to simulate the effect of the range of soil particle fractions found naturally.

- Critical examination of the results indicated that the performance of the surfactant solutions in oil removal was relatively dependent on properties such as foaming ability, soil particle size distribution and nature of oil.
- All the surfactant solutions showed approximated constant oil removal of more than 95 and 90 % from the non-weathered and weathered samples of Soil – 1. The greater oil removal was attributed to the interaction of surfactant/soil (such as sorption of surfactant to soil) and surfactant/oil (such as interfacial tension reduction and emulsifications), which dominates the interaction of oil/soil.
- The disparity in crude oil and heavy oil removal from Soil – 1, Soil – 3, Soil – 4 and Soil – 5 was due to the resulting complex nature of crude oil after weathering. The disparities were more pronounce as the soil particle fraction is increasing. The low oil removal from the larger fractions of the weathered soil samples was due to the surface roughness of the soil. As the soil samples have groves and cavities, the oil will stick inside the soil pores and reduce the surface interaction with the surfactants.
- Surfactant with low molecular weight, and less bulk and complex hydrocarbons chains was observed to have greater oil removal. Saponin has the largest weight and



complex structure followed by rhamnolipid and then SDS, oil removal from Soil – 3, Soil – 4 and Soil – 5 was in the following descending order: SDS<sub>n</sub>, S<sub>n</sub> and/or R<sub>n</sub> and SDS<sub>w</sub>, S<sub>w</sub> and R<sub>w</sub>. The order of oil removal appears to be the same as order of surfactant foaming stability and sorption to soil.

- Washing solutions showed a considerable oil removal as the temperature is increased.
- The slight increase in oil removal from the non-weathered samples during the effect of volume/mass ratio may be due to the formation of emulsions. This is because increasing the concentration of aqueous surfactant solutions and the volume ratio of surfactant solution to crude oil would lead to the formation of emulsions. Emulsions aiding oil removal will be favourable for fresh contaminated soils. The maximum oil removal obtained with 20 cm<sup>3</sup> solutions suggested that such a volume is enough to create the displacement of oil from the weathered soil samples.
- The rhamnolipid with 99% purity removed greater amount of oil below the CMC value. However, depending on the cost of purifying the fermentation broth to 99 %, the fermentation broth may be considered a better option since oil removal at 0.1 %-mass was the same with the 99% rhamnolipid.
- After storing the weathered crude oil contaminated for six months and washed, oil removal did not change but for the non-weathered samples, they was reduction in crude oil removal suggesting the effect of weathering. This weathering may persist if the soil sample is kept for longer time.
- The used of seawater represent a real life situation, since fresh water may not be available on the site when handling large volume of contaminants. The seawater solutions enhance the removal of crude oil and heavy oil from Soil – 4 to about 40 % and 70 % respectively. The electrolyte in seawater reduces the electrostatic repulsion between the similar ionic heads of aqueous solution of surfactants. For Soil – 1, it is not surprising to have similar oil removal using either distilled water or seawater. This could be explained by understanding that Soil – 1 had a large surface area, which is associated with large electric charges. This negative charge will counteract those ions contributed by the electrolyte thereby resulting to a washing solution that is similar to distilled water.
- The applicability of this study would not only be on the treatment of soils contaminated by petroleum oil spills, but in managing contaminated soils generated through drilling operations that are improperly disposed.

### **5.1.12 Soil washing: air sparging assisted stirred tank reactor**

The results of oil removal from 200 g of the contaminated soil using the air-sparging reactor are summarized herein.

- It was found out that the removal of oil from the non-weathered soil samples could be achieved at the first and second parameter levels tested.
- Oil removal at the different points of the reactor was approximately the same, which indicated uniform mixing.
- The removal of crude oil from the non-weathered soil samples was more effective than that of the heavy oil. The oil removal was not only dependent on the physiochemical characteristics of the washing media but was relatively dependent on the floating of the contaminated soil.
- Rhamnolipid that have a sorption 75% and less foam stability showed an oil removal of about 80% which was comparable to that of SDS at the third and fourth parameter levels tested.
- The heavy oil removal was more significant with seawater prepared solutions, which showed more than 40% in comparison with the distilled water prepared solutions at the first and second parameter levels tested.
- This approach of soil washing was observed to be the most effective; therefore field test is suggested to access the efficiency of these surfactant solutions and water.

### **5.1.13 Soil washing: column**

Soil washing study was conducted in glass columns to simulate the in-situ technique. The removal of crude oil and heavy oil was investigated using solutions of rhamnolipid, saponin and SDS prepared in either distilled water or seawater.

- Crude oil removal from the non-weathered and the weathered soil samples with distilled water was about 40 and 20% respectively. This removal was observed to be twice the amount removed during the washing of the heavy oil contaminated soil. Rhamnolipid and saponin showed about 80% and 60% crude oil removal from the non-weathered samples with 0.1%-mass solutions. This concentration is about 5 fold greater than the CMC of rhamnolipid that showed the greatest oil removal.
- With the low surfactant concentrations tested, the effect of both emulsification and solubilization mechanisms were negligible. Mobilization due to the reduction of interfacial tension of oil/water system, which is responsible for the displacement of

oil droplets from soil, is behind the oil removal.

- The surfactant molecular weights and structures are in the following increasing order: SDS, rhamnolipid, and saponin also crude oil removal was in the reverse order.
- As the flow rate increases, the oil removal decreases. Maximum oil removal was achieved at 2 cm<sup>3</sup>/minute corresponding to 20 minutes residence time. The mechanical effect of flow checked at 32 cm<sup>3</sup>/minute for rhamnolipid solution does not influence oil removal in the column but the longer the retention time of the surfactants in the column will influenced the oil removal positively.
- At higher PV, rhamnolipid crude oil removal was better than SDS and distilled water. Its removal was asymptote to the x-axis indicating that an increase in PV beyond 50 would not significantly enhance the oil removal. Whereas SDS indicated that more crude oil would have been removed if the PV were to be increased above 70.
- At high temperature of about 35<sup>0</sup>C to 50<sup>0</sup>C distilled water washing shows a more linear relationship with crude oil removal. Comparing the efficiency of rhamnolipid and SDS at 20<sup>0</sup>C indicate the differences in oil removal between these two surfactants were insignificant. This temperature was chosen based on cost and other treatment factors such as emission gases. Therefore, 50<sup>0</sup>C washing is economically and environmentally disadvantaged.
- The removal of the heavy oil was almost half to that of crude oil, this confirms the adverse effect of high viscosity of oil during soil washing process. Oil with high viscosity will increase the adherence or binding with soil. This may further reduced the mobility of oil and thereby slowing down the oil removal process.
- With seawater prepared solutions, there was a reduction of about 20-30 % crude oil removal in comparison with solutions prepared with distilled water. This reduction may be attributed to the resulting effect of seawater during surfactant solution preparations such as precipitates. Precipitation of rhamnolipid increases as concentration of is increased which will lead to loss of surfactant concentration.
- The oil removal in this study was comparable with those that exist in the literature. This experiment was repeated twice, the repeatability and experimental error were found within the range  $\pm 4$  and  $\pm 3$  %, respectively.

#### **5.1.14 GC/MS**

The GC/MS study was conducted to understand if there is preferential removal of crude oil components from soil using the surfactant solutions. These results provide important information for the selection of surfactants used to remove crude oil from contaminated soils. This study shows that biosurfactants can be equally as efficient at removing oil from soil as synthetic surfactants. Further, biosurfactants can preferentially remove certain aromatic groups, which may be desirable for more rapid soil remediation. The relative loss of the different hydrocarbon components through the soil washing process are summarised below.

- Rhamnolipid and SDS are the most, and equally, efficient at removing crude oil from soil, while saponin is the least efficient.
- Rhamnolipid and SDS remove a relatively greater proportion of the aliphatic components. Saponin removes aliphatic and aromatic components in equal proportions.
- Rhamnolipid and Saponin are more efficient at removing the naphthalenes than SDS. Saponin is the most efficient at removing the phenanthrenes.

#### **5.1.15 Soil washing: optimization**

The Taguchi experimental design method was used to determine optimum condition, access the robustness or stability and the reproducibility of the soil washing method for possible field scale applications.

- The experimental plan provides an economical way of simultaneously studying the effects of many parameters on process mean and variance. The Taguchi method is a fractional factorial design that can show process variability and stability. Most importantly, values determined at optimum conditions in the laboratory are reproducible in industrial application.
- Results gained from these studies indicated that temperature and concentrations of surfactant solutions were the most influential parameters.
- With the Taguchi method the optimum removal of crude oil with rhamnolipid and saponin was observed to be about 80 %.
- The confirmatory experiment and the predicted crude oil removal showed that the washing method was stable for all the biosurfactant solutions except aescin and lecithin which show predicted crude oil removal out of range.

- As error level is increased from  $\pm 1 \%$  to  $\pm 10 \%$ , stability of the washing method reduces.
- Although the cost analysis is not given, this work suggested a field scale investigation to assess the surfactants performances in removing crude oil from both weathered and non-weathered contaminated soil samples.

## 5.2 Recommendations for future work

This work embraced several experimental techniques in an attempt to wash oil-contaminated soils through different washing settings. The removal of oil from the air sparging assisted stirred tank reactors showed promising oil removal, thus future work can be carried out in field scale. In this sense, the use of seawater and surfactants that have better foaming will be favourable. However, the materials characterization such as those in Section 3.1 should be conducted at different systems such soil/water, soil/oil and oil/water.

A real contaminated soil from crude oil drilling sites could be studied with rhamnolipid. This will be most appreciated in areas where on-shore operations are most predominant, due to the easy access of the crude oil into the immediate environment.

The quantification of the amount of the different crude oil components remaining in the washed soil with the analysis of GC/MS is another area of surfactant oil removal from soil that need to be developed. Researches towards this aspect will further remove the fear of spending money in surfactant solution characterizations. However, with the idea that different surfactants have preferential abilities in removing the different components of crude oil from contaminated soils, this approach will be useful in blending various surfactants for a particle kind of crude oil removal from soil.

It is important to recover the surfactant solutions from the wastewater after soil washing for reuse so that the process will be more economical. Crystallization or precipitation method with monovalent or multivalent counterions could be used to recover ionic surfactants from concentrated surfactants solution. This approach could be applied in recovering the ionic surfactants employed in this study following the method described in Brant et al. (1989). The recoveries of the spilled or wasted crude oil is another area where research could be focused. This will be of major concern in the field of

environmental management and remediation, since the approach of waste material recycling is sustainable compliance.

Further experimental work on Taguchi method can be tested for the other washing settings, the cost analysis should be also be incorporated since the experimental plan provides an economical way of simultaneously studying the effects of many parameters on process mean and variance.

# Appendices

## A1 List of publications

1. Urum, K., T. Pekdemir and S. Grigson, A comparison of the efficiency of different surfactants to remove crude oil from contaminated soils (Chemosphere – Accepted).
2. Urum, K., T. Pekdemir and M. Çopur, Screening of biosurfactants for crude oil contaminated soil washing (Journal of Environmental Eng. and Science – in press).
3. Urum, K., T. Pekdemir, D. Ross and S. Grigson, Treatment of petroleum hydrocarbon contaminated soil using biosurfactants in air sparging assisted stirred tank reactors (Chemosphere – in press)
4. Urum, K., T. Pekdemir and M. Çopur, Surfactants treatment of crude oil contaminated soils, Journal of Colloid and Interface Science, 276, 2004, pp 456-464.
5. Urum, K., T. Pekdemir and M. Çopur, Optimum conditions for washing of crude oil-contaminated soil with biosurfactant solutions, Process Safety and Environmental Protection 81 (3), 2003, pp. 203-209.
6. Urum, K., T. Pekdemir and M. Çopur, Emulsification of crude oil - water systems using biosurfactants, Process Safety and Environ. Protection, 83, 2005, pp 38-46.
7. Urum, K., and T. Pekdemir, Evaluation of biosurfactants for crude oil contaminated soil washing, Chemosphere, 57, 2004, 1139-1150.
8. Urum, K., and T. Pekdemir, Solubilization of Ekofisk crude oil in aqueous biosurfactant solutions (*under review*)

## Conferences

1. Four papers accepted for the 7<sup>th</sup> World Congress of Chemical Engineering in Glasgow, UK, July 10-14, 2005.
2. Biosurfactant enhanced treatment of soils contaminated by petroleum oils using stirred tank reactors, First International Symposium on Process Intensification and Miniaturization, 18th - 21st of August 2003, Newcastle University, UK
3. Biosurfactant enhanced treatment of soils contaminated by petroleum oils in a packed column, First International Symposium on Process Intensification and Miniaturization, 18th - 21st of August 2003, Newcastle University, UK

## A2 Mass Spectrometric study for aromatic hydrocarbons

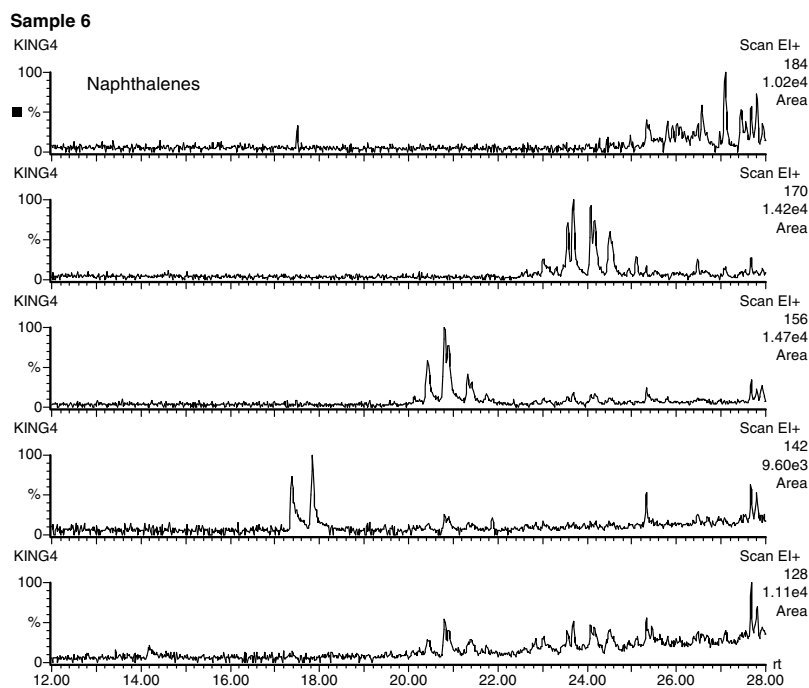


Figure A.1. GC/MS chromatograms of sample washed with 0.1 %-mass of rhamnolipid solution at  $m/z$  128, 142, 156, 170 and 184 for naphthalene aromatic hydrocarbon

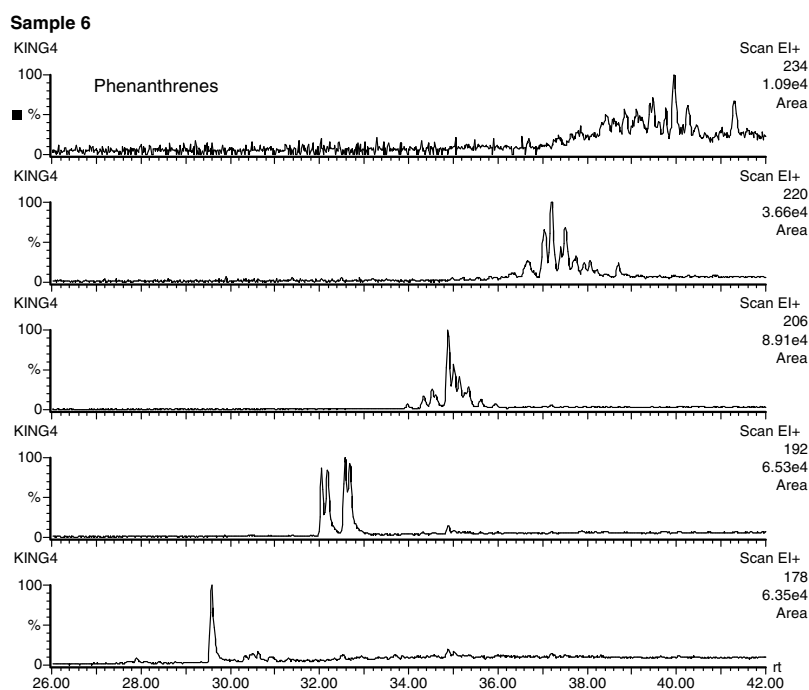


Figure A.2. GC/MS chromatograms of samples washed with 0.1 %-mass rhamnolipid at  $m/z$  178, 192, 206, 220 and 234 for phenanthrenes aromatic hydrocarbon



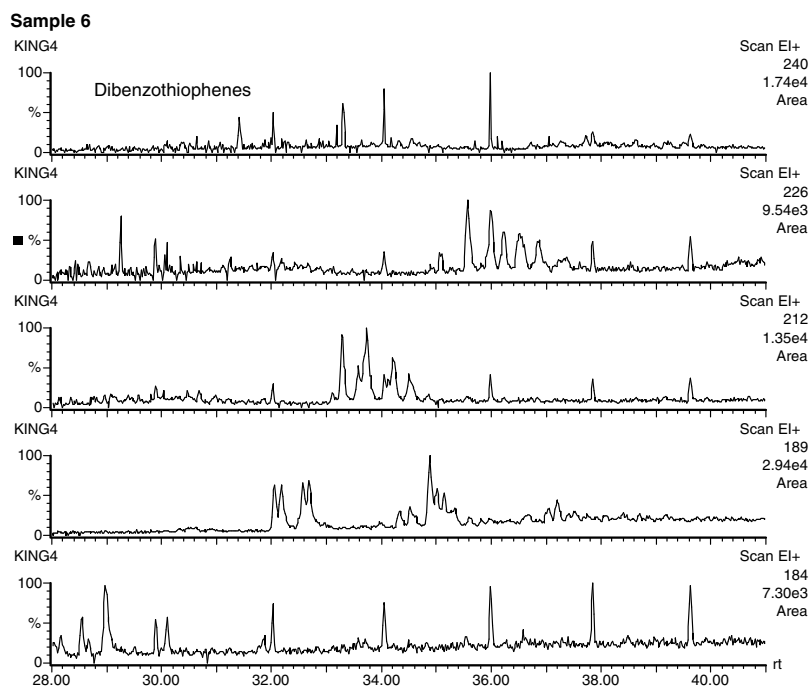


Figure A.3. GC/MS chromatograms of samples washed with 0.1 %-mass rhamnolipid at m/z 184, 198, 212, 226 and 240 for dibenzothiophenes aromatic hydrocarbon

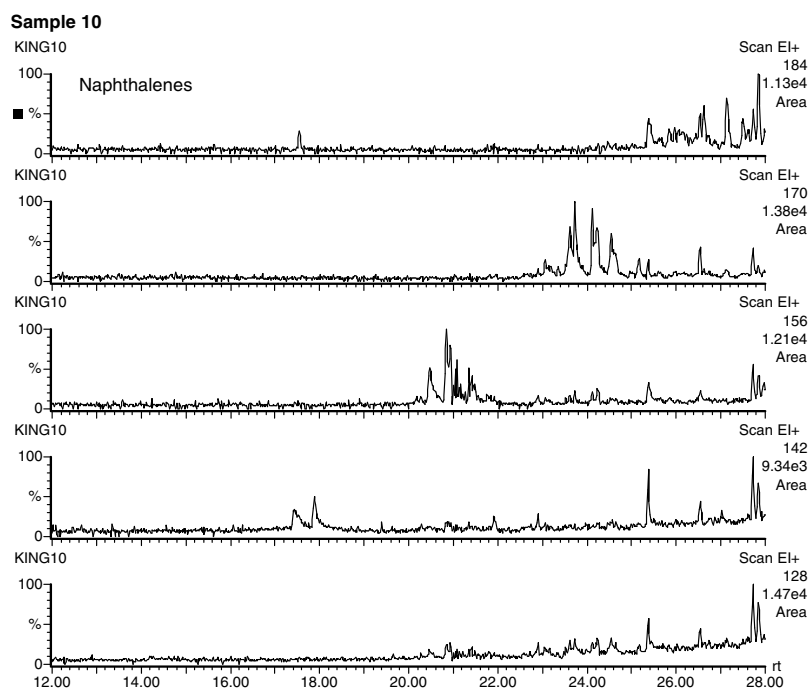


Figure A.4. GC/MS chromatograms of samples washed with 0.1 %-mass saponin at m/z 128, 142, 156, 170 and 184 for naphthalene aromatic hydrocarbon.

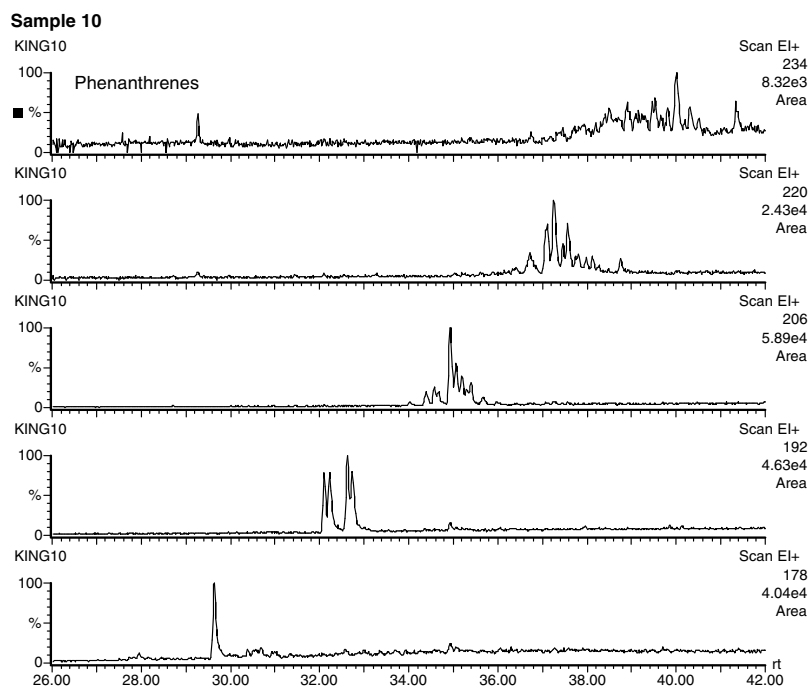


Figure A.5. GC/MS chromatograms of samples washed with 0.1 %-mass saponin at m/z 178, 192, 206, 220 and 234 for phenanthrenes aromatic hydrocarbon.

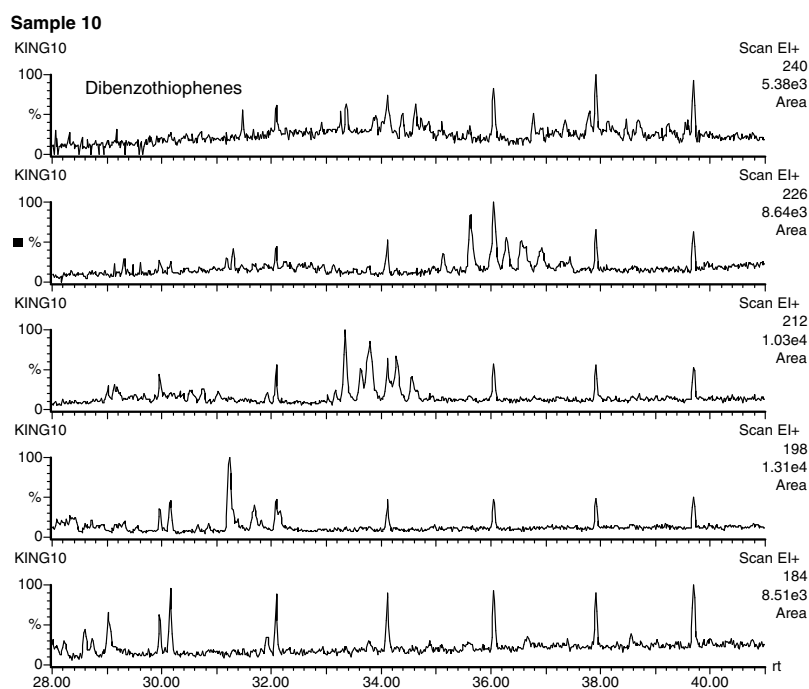


Figure A.6. GC/MS chromatograms of samples washed with 0.1 %-mass saponin at m/z 184, 198, 212, 226 and 240 for dibenzothiophenes aromatic hydrocarbon.

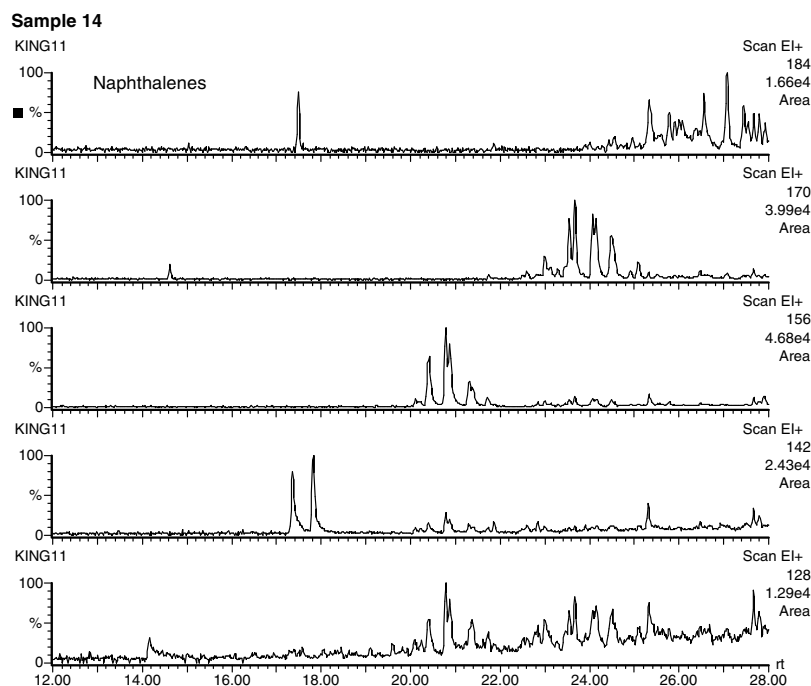


Figure A.7. GC/MS chromatograms of sample washed with 0.1 %-mass SDS solution at  $m/z$  128, 142, 156, 170 and 184 for naphthalene aromatic hydrocarbon

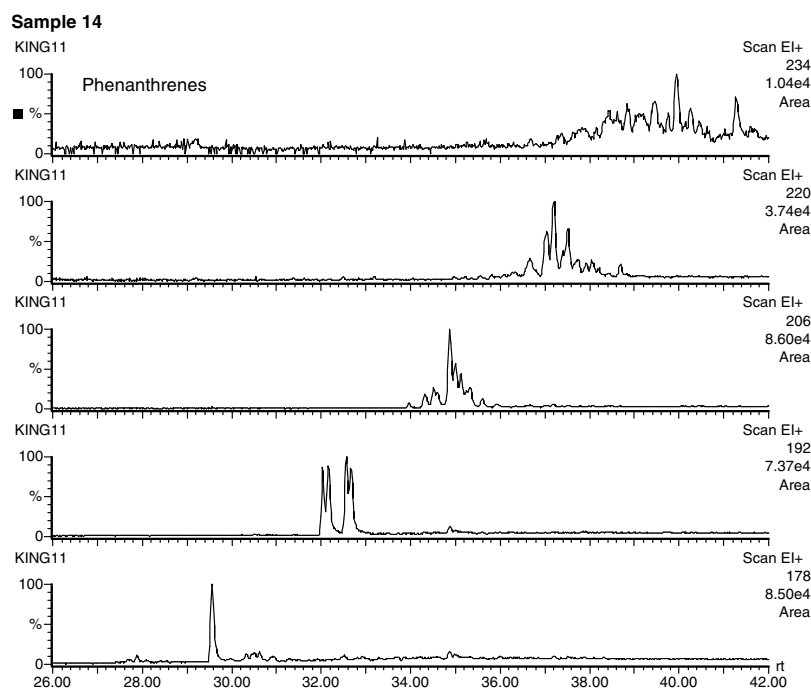


Figure A.8. GC/MS chromatograms of sample washed with 0.1 %-mass SDS solution at  $m/z$  178, 192, 206, 220 and 234 for phenanthrenes aromatic hydrocarbon

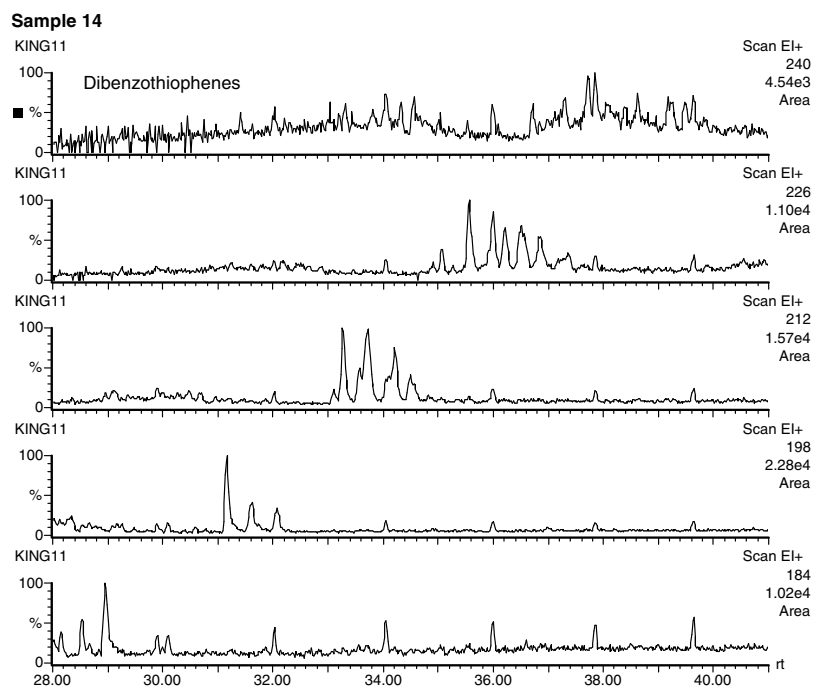


Figure A.9. GC/MS chromatograms of sample washed with 0.1 %-mass SDS solution at m/z 184, 198, 212, 226 and 240 for dibenzothiophenes aromatic hydrocarbon

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